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# IDENTIFICATION OF SELECTED FIBERS BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

by
**Rosa Linda Riel-Bagalawis**

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**U.S. Army Research, Development and Engineering Command**
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A pyrolysis-gas chromatographic method was developed in 2000 to characterize military fibers and fabrics. As the performance and durability of materials relate to their fiber composition, a sensitive and reliable method for the identification of fibers became necessary. The method was further improved by incorporating a mass spectrometer as a detector to ensure accurate component identification from the pyrolyzates. Pyrograms and gas chromatographic analysis are highly reproducible. This analytical method is reliable for the characterization of fibers.

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## Preface and Acknowledgements

This analytical work of fibers supports projects in the Engineering, Prototype and Performance Evaluation Team, Army Soldier System Engineering Team and Materials Integrated Team of the Individual Protection Directorate (IPD), U.S. Army Research, Development and Engineering Command (RDECOM), Natick Soldier Center, Natick, Massachusetts. This study also supports projects of the Aerial Delivery Engineering Support Team of the Airdrop/Aerial Delivery Directorate and the 21st Century Fabric Structures Team of the Shelter Directorate belonging to the same Command.

Identification of fibers using a Pyrolysis-Gas Chromatography-Flame Ionization Detector (Py-GC-FID) was conducted by comparing gas chromatographic (GC) profiles of the pyrolysis products of the sample to those of known standards. In 2003, the addition of a Mass Spectrometer (MS) detector to the gas chromatograph (GC) enabled us to confirm the presence of fibers not only from their GC profiles but also by their major pyrolysis products.

The research was conducted at the U. S. Army RDECOM during the period of September 2000 through December 2003 under program element 423012.12 and project OMA.

The author would like to thank Walter Yeomans and Joel Carlson for their help in the configuration of the gas chromatography-mass spectrometry (GC-MS) software after the installation of the pyrolysis apparatus on the new GC-MS.

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# IDENTIFICATION OF SELECTED FIBERS BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

## Introduction

The U. S. Army utilizes a large number of fibers and fabrics in support of clothing, headgear and tent materials. As the performance and durability of materials relate to their fiber content, a sensitive and reliable method for the identification of fibers became necessary.

Fibers cannot be analyzed by direct gas chromatography and mass spectrometry because they are often blended polymers that are non-volatile. They have to be broken into simpler components that are volatile for analysis.

Pyrolysis is a chemical process whereby thermal energy breaks down large molecules into smaller fragment molecules in the absence of oxygen. Pyrolysis coupled with gas chromatographic (Py-GC) separation of the volatile fragments provides a simple analytical method that can be used to characterize the nature and identity of the fibers and fabrics of military interest. The addition of mass spectrometry to the GC allows one to identify the individual fragments (Py-GC-MS) providing a powerful tool that can be applied to a wide range of chemical problems (Hardin, I., 1996).

The pyrolysis profile is characteristic of a particular sample either in the appearance of unique components or in the relative distribution of the products (Irwin, 1982).

From 2000 - 2002, Natick used Py-GC techniques for the characterization of fibers from clothing, headgear/helmet liners, parachutes, tent materials and other garments. Using Py-GC equipped with a flame ionization detector, we obtained pyrograms (graphs with peaks and retention times) from only a few fibers and based on references, we were able to identify the fibers after matching them to pyrogram profiles in the standards.

For fiber material with less than 5% of additives/finish, sample preparation is not needed for this analysis. Otherwise, extraction of the nonfibrous materials may be necessary as is the case with the analysis of PVC-coated polyester.

In more recent studies, Natick has combined pyrolysis-gas chromatography (Py-GC) with mass spectrometry (MS). For qualitative confirmation purposes, to ensure that the appropriate pyrogram represented a specific fiber, the mass spectrometer was used to identify the major fragments through a mass spectral library search.

Since these processes Py-GC-MS are characteristic of the polymers involved, and are highly reproducible, it becomes relatively straightforward to identify a polymer based on the identity of its pyrolysis products (Wampler and Zawodny, 1999).

Polyolefins such as polyethylene and polypropylene generate many oligomers, creating a characteristic pattern that becomes readily recognizable. Polyethylene is a long, aliphatic polymer; its pyrolytic products are normal hydrocarbons, including alkanes, alkenes and dienes, which produce the pattern of triplet peaks in the pyrogram of polyethylene. The effect of having the methyl branches observed in polypropylene is easily discerned in the pyrogram. The large peak of dimethyl heptene, trimer of propylene is seen in the pyrogram of poly propylene (Wampler and Zawodny, 1999).

By reviewing the structure of a fiber/polymer, the pyrolysis products can be predicted as in the cases of Nomex® and Kevlar®. The only difference between these two polymers is that in Kevlar®, the amino and carboxyl groups are in para positions on the aromatic rings while in Nomex®, the amino and carboxyl groups are in the meta positions of the aromatic rings. In the same way, any fiber with a cellulosic structure can be projected to yield pyrolysis products similar to those of cotton.

Table 1. on the following pages shows molecular structures and the pyrolysis products of selected fibers as cited by references and other products as predicted based on the molecular structures of a few fibers.

Table 1. *Molecular Structure of Fibers and Their Major Pyrolysis Products*

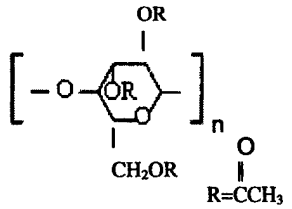
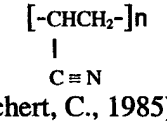
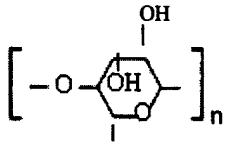
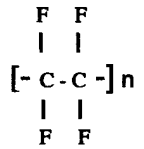
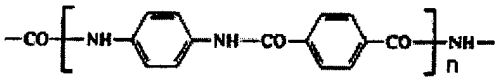
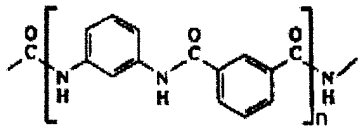
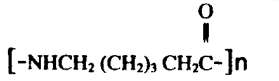
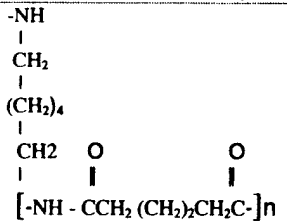
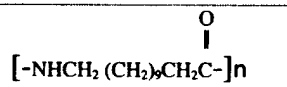
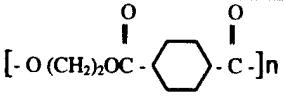
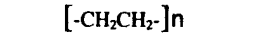
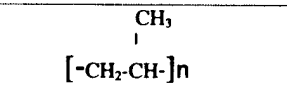
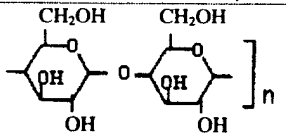
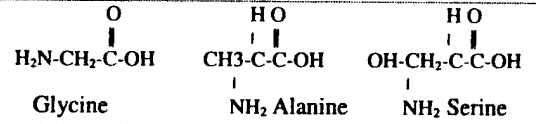
| Fiber ID | Molecular Structure | Major Pyrolysis Products |
|---|---|---|
| Acetate (Cellulose Acetate) |  (Pouchert, C., 1985) | Acetic anhydride; acetic acid; glycolaldehyde (Hardin, I. & Wang, X. 1989) |
| Acrylic (Polyacrylonitrile) |  (Pouchert, C., 1985) | Acetonitrile; acrylonitrile or propenenitrile (Wampler, T. & Zawodny, C., 1999) |
| Cotton |  (Segal, L. & Wakelyn, P. J., 1985) | Carbon dioxide; oxirane; furan; acetone; glycolaldehyde; acetic acid; 1-hydroxy 2-propanone; acetic anhydride; furfuraldehyde (Hardin, I., 1996) |
| Gore-Tex® (PTFE) |  (Stecher, P., Finkel, M., Siegmund, O. & Szafranski, B., 1960) | Tetrafluoroethylene (Wampler, T. & Zawodny, C., 1999) |
| Kevlar® |  (Yang, H., 1993) | Benzene; aniline; benzonitrile; amino compound, carbonitriles (Wampler, T., 1995); 1,4-benzenediamine (projected) |
| Nomex® |  (Yang, H., 1993) | Benzene; toluene; aniline; benzonitrile; amino compound; carbonitriles (Wampler, T., 1995); 1,3-benzenediamine (projected) |

Table 1. *Molecular Structure of Fibers and Their Major Pyrolysis Products (Cont'd)*

| Fiber ID | Molecular Structure | Major Pyrolysis Products |
|---|---|---|
| Nylon 6 |  (Pouchert, C., 1985) | Caprolactam (CDS Applications Lab Personnel, 1995) |
| Nylon 66 |  (Pouchert, C., 1985) | Cyclopentanone; hexamethylene diamine (Wampler, T., 1995) |
| Nylon 12 |  (Pouchert, C., 1985) | Amides; hydrocarbons; mononitriles (CDS Application Lab Personnel, 1995) |
| Polyester |  (McIntyre, J. E., 1985) | Benzene; benzoic acid; biphenyl; vinyl terephthalate (Hardin, I, 1996); benzene, vinyl benzoate, benzoic acid, biphenyl (Wampler, T., 1995) |
| Polyethylene |  (Pouchert, C., 1985) | 1,9-decadiene; 1-decene; 1-decane (C10 up to C39) (Wampler, T., 1995) |
| Polypropylene |  (Pouchert, C., 1985) | Methyl branched hydrocarbons: trimer, tetramer, etc. Dimethylheptene (Wampler, T. & Zawodney, C., 1999) |
| Rayon |  (Dyer, J. & Daul, G., 1985) | Carbon dioxide; acetic acid; glycolaldehyde; 1-hydroxy-2-propanone; furaldehyde; 1,2-cyclopentanedione (projected) |
| Silk |  Glycine NH2 Alanine NH2 Serine Plus other amino acids (Pouchert, C., 1985) | Benzene, toluene, picoline (Irwin, 1982) Carbon dioxide; aromatic compound; phenol (CDS Application Lab Personnel, 1995) |
| Wool | C – 50%; O – 22 to 25%; N – 16 to 17%; H – 7%; S – 3 to 4% (Bergen, V., 1948) | Carbon dioxide; methane; hydrogen sulfide; Carbon disulfide (Hardin, I., 1996) |

## MATERIALS AND METHODS

*Standards*

Standard fibers of acetate, acrylic, cotton, Gore-Tex®, Kevlar®, Nomex®, nylon 6, nylon 66, nylon 12, polyester, polyethylene, polypropylene, rayon, silk and wool were obtained from our collection here at Natick. Approximately a microgram of each standard was required for each study.

*Samples*

A microgram of each sample was required and the number of samples varied from 2 to 23.

*Quality Assurance/Quality Control (QA/QC)*

Prior to any analysis, the pyrolysis chamber was auto-cleaned by setting it to 1200°C for 20 seconds as recommended by the equipment manufacturer. An instrument blank was run on the GC-MS to ensure that the instrument was clear of all interferences.

Laboratory blanks, in which the pyrolyzer was operated with no sample present, was used to ensure that each analysis was free of contamination. Any blank sample showing a positive concentration resulted in the qualification of the analytical sample. In these studies, no contaminated blanks were observed.

Standard duplicates were also used to ensure the reproducibility of the analytical method. In the event that the pyrogram failed to yield reproducible results, the analytical instrument was diagnosed and repaired or sent out for preventive maintenance or repair.

Auto-cleaning of the pyrolysis chamber was conducted after every sample. Standards were run every 12 hours of operation.

*Pyrolysis-Gas Chromatography (Py-GC)*

The first Py-GC technique was developed using a Model AS 2500 Pyrolyzer equipped with an auto sampler manufactured by CDS Analytical connected to a Hewlett-Packard Model 5890A Gas Chromatograph. The pyrolyzer chamber/oven and the auto sampler and gas chromatograph were all computer controlled. About one microgram of a sample was placed into

20 seconds. The pyrolyzer interface temperature that transferred the pyrolyzates to the GC was set at 300$^0$C. The probe was automatically cleaned after every run at 1200°C for 20 seconds.

The carrier gas Helium flowing 5 mLs per minute swept the volatile through the splitless inlet of the gas chromatograph at a temperature of 300$^0$C and into a Hewlett-Packard HP-5 column of fused silica, 30-meters long with 0.53 mm I.D. coated with 5%-Phenyl-methylpolysiloxane up to the detector. The oven temperature was initially maintained at 40$^0$C for one minute and then it was temperature programmed at the rate of 6$^0$ per minute up to a final temperature of 300$^0$C for 15 minutes. Hydrogen and compressed air were used for the flame ionization detector that was maintained at 275$^0$C.

Peak heights, areas and retention times for the standards and samples were measured and sequentially saved by a computer. The pyrograms of the samples were compared with those of the standards. The characterization of the sample fibers was conducted by comparing the sample pyrograms with those of the standards.

*Pyrolysis-Gas Chromatography-Mass Spectrometry(Py-GC-MS)*

In recent studies, the Model AS 2500 Pyrolyzer manufactured by CDS Analytical was combined with a Gas Chromatograph Model 6890N- Mass Spectrometer Model 5873N in order to enhance the selectivity and sensitivity of the analytical method. The column was changed from HP-5 to HP-5ms column of bonded 5%-Phenyl-methylpolysiloxane, 30-meters long and 0.25 mm I.D. The carrier gas was helium but hydrogen and air were no longer required with the elimination of the Flame Ionization Detector from the method. The chromatographic conditions described above were used on the GC-MS except the flow rate of helium was reduced to 1 mL per minute to accommodate the requirements of the mass spectrometer. The detector temperature was 280$^0$C. The inlet flow split ratio was 50:1.

## Results

The pyrolysis products of the standard fibers were identified and their molecular weights were obtained searching the NIST Mass Spectral Library (Stein, Levitsky, Fateev, Tchekhovski & Mallard, 2000). See Table 2. below.

Table 2. *Standard Fibers, Major Pyrolysis Products Identified and their Molecular Weights*

| Fiber ID | Major Pyrolysis Products Identified | Mol. Wt. |
|---|---|---|
| Acetate (Cellulose acetate) | Acetic acid | 60 |
| | Methyl acetate | 74 |
| Acrylic (Polyacrylonitrile) | Propenenitrile (acrylonitrile) | 53 |
| Cotton (cellulose-based) | Carbon dioxide | 44 |
| | Glycolaldehyde | 60 |
| | 1-hydroxy-2-propanone | 74 |
| | Furfuraldehyde | 96 |
| | 2-hydroxy-2-cyclopentene-1-one | 112 |
| Gore-tex® (Teflon) | Tetrafluoroethene or tetrafluoroethylene | 100 |
| Kevlar® (p-phenylene terephthalamide) | Aniline | 93 |
| | Benzonitrile | 103 |
| | 1,4-benzenediamine | 108 |
| Nomex® (m-phenylene isophthalamide) | Aniline | 93 |
| | Benzonitrile | 103 |
| | 1,3-benzenediamine | 108 |
| Nylon 6 | Caprolactam | 113 |
| Nylon 66 | Cyclopentanone | 84 |

Table 2. *Standard Fibers, Major Pyrolysis Products Identified and their Molecular Weights (Cont')*

| Fiber ID | Major Pyrolysis Products Identified | Mol. Wt. |
|---|---|---|
| Nylon 12 | 2-propenenitrile | 53 |
| | Nonene | 126 |
| | Decanenitrile | 153 |
| Polyester (PET) | Benzene | 78 |
| | Benzoic acid | 122 |
| | Biphenyl | 154 |
| Polyethylene | 1,9-decadiene | 138 |
| | Decene | 140 |
| | Decane | 142 |
| | Triplets of –diene, -olefin & n-alkane, C10-C39 | |
| Polypropylene | 2-methyl-1-pentene | 84 |
| | 2,4-dimethyl-1-heptene | 126 |
| Rayon (cellulose-based) | Carbon dioxide | 44 |
| | Acetic acid | 60 |
| | Glycolaldehyde | 60 |
| | 1-hydroxy-2-propanone | 74 |
| | Furaldehyde | 96 |
| Silk (protein) | Carbon dioxide | 44 |
| | Acetyl hydrazide | 74 |
| | Ammonium carbamate | 78 |
| | Phenol | 94 |
| | Methyl phenol | 108 |
| Wool (sulfur protein) | Carbon disulfide | 76 |
| | Ammonium carbamate | 78 |
| | Toluene | 92 |
| | Phenol | 94 |
| | 4-methyl phenol | 108 |

On the pages that follow, Figures 1 to 30 show pyrograms of selected standard fibers and mass spectra of their major pyrolysis products. By comparing the pyrogram and the major pyrolysis products of a sample with the pyrogram and the major pyrolysis products of the known standard, the unknown fabric can be identified. The following conclusions can be made using the data collected. Figures 31 and 32 on the following pages show a pyrogram of an unknown fabric material sample and a mass spectrum of benzoic acid, respectively. The pyrogram of the sample and the major pyrolysis product, benzoic acid are comparable to that of polyester. Figures 33 and 34 show a pyrogram of an unknown helmet liner sample and mass spectrum of caprolactam, the major pyrolysis product, respectively. The pyrogram and the major pyrolysis products are comparable to those of nylon 6. Figure 35 shows a pyrogram of a tent material sample after extraction of polyvinyl chloride. It is similar to that of polyester. Figure 36 is a mass spectrum of benzoic acid, a major pyrolysis product of polyester; therefore the tent material sample is a mixture of polyester and polyvinyl chloride. Figure 37 shows a pyrogram of an unknown foamy inner layer of a headgear sample. The profile is similar to that of polyethylene. One of the major pyrolysis products is 1-decene as shown by Figure 38. The other pyrolysis products were 1,9-decadiene and decane, therefore it is polyethylene.

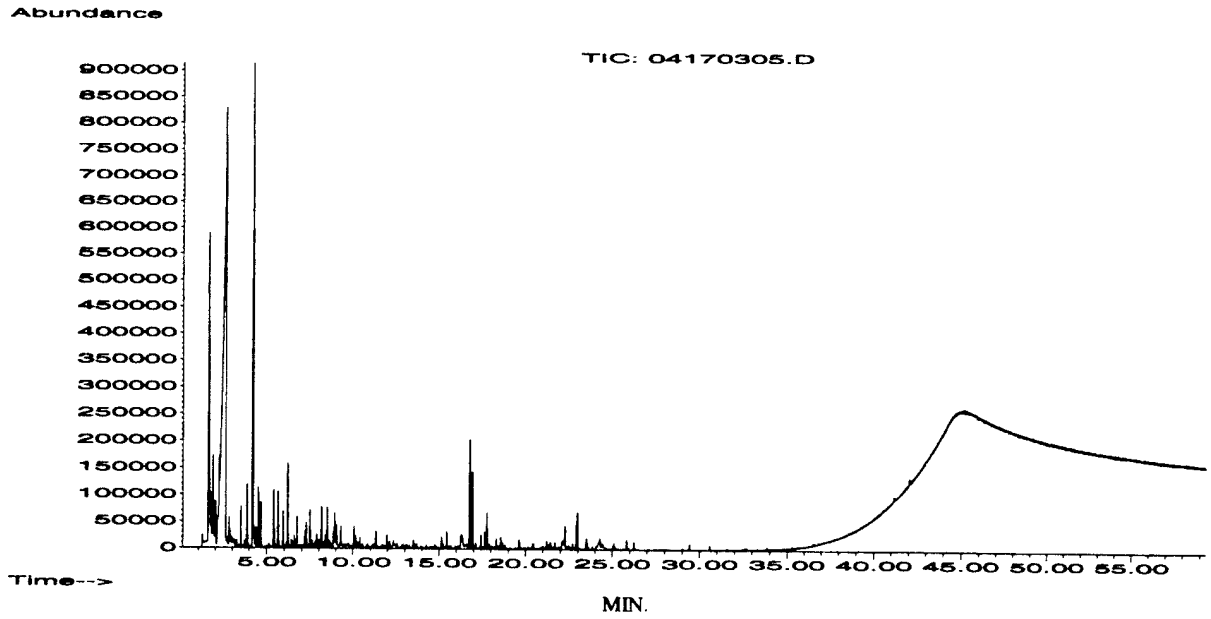



*Figure 1.* Pyrogram of cellulose acetate

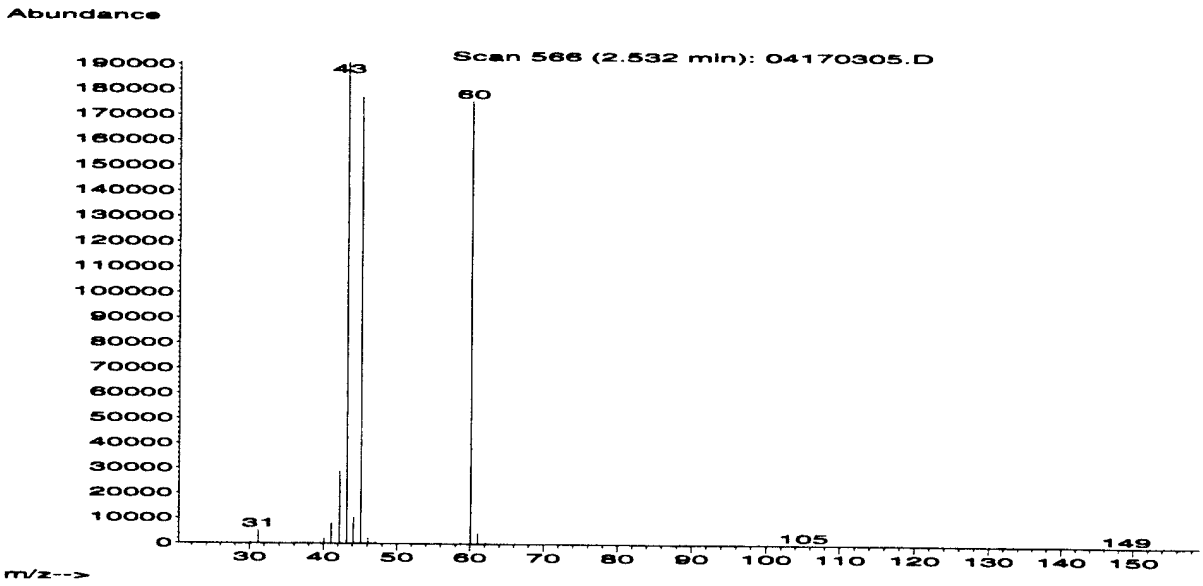



*Figure 2.* Mass spectrum of acetic acid

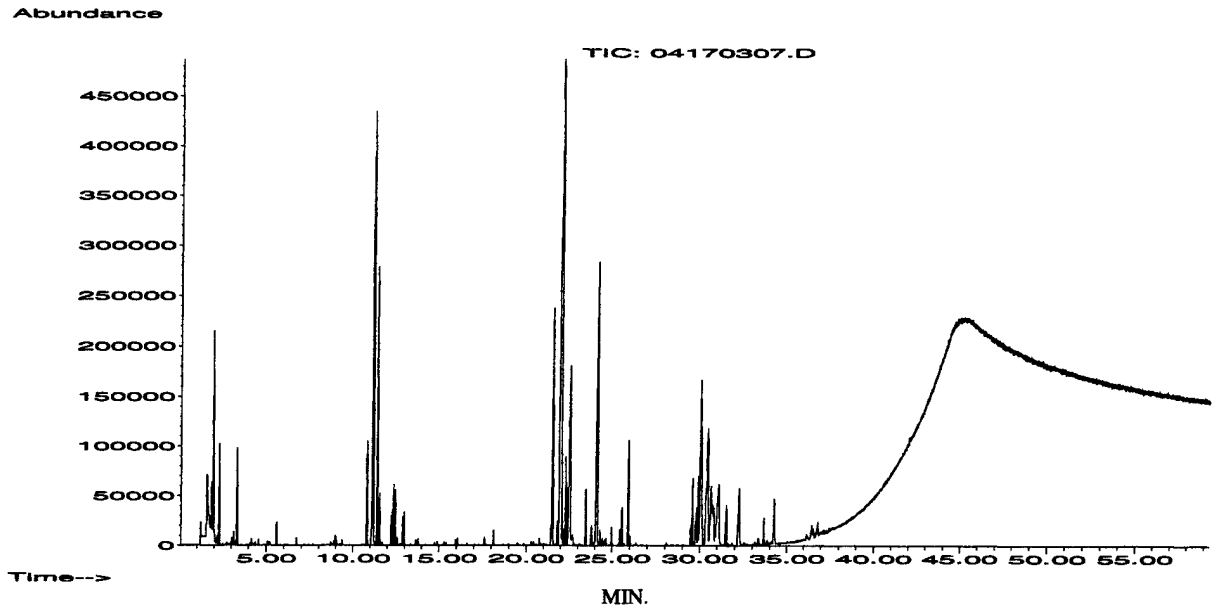



*Figure 3.* Pyrogram of polyacrylonitrile

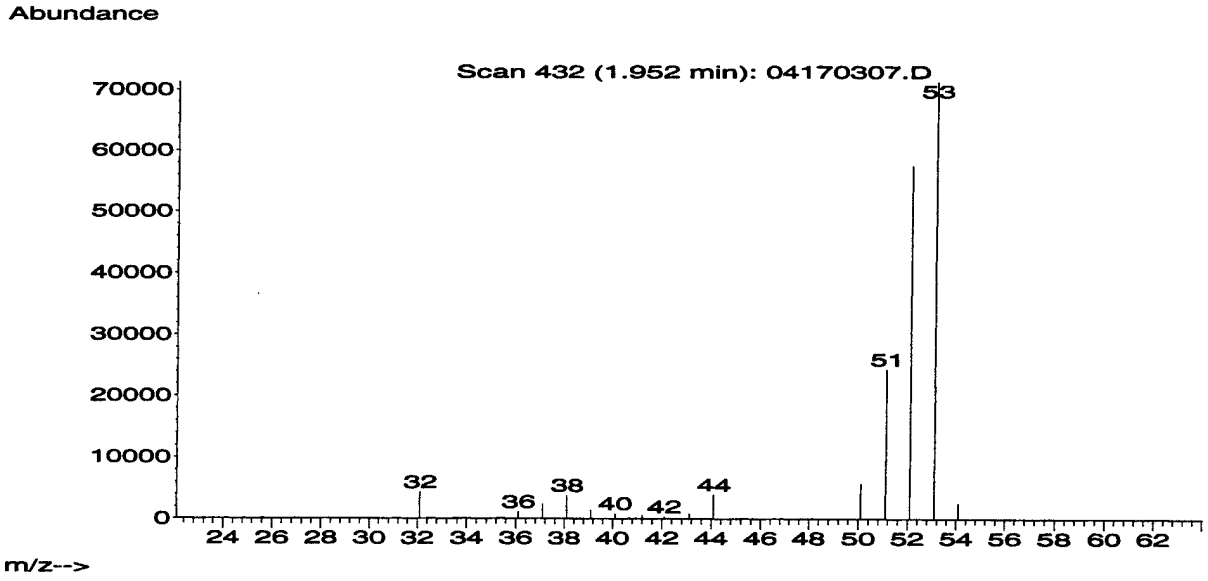



*Figure 4.* Mass spectrum of acrylonitrile

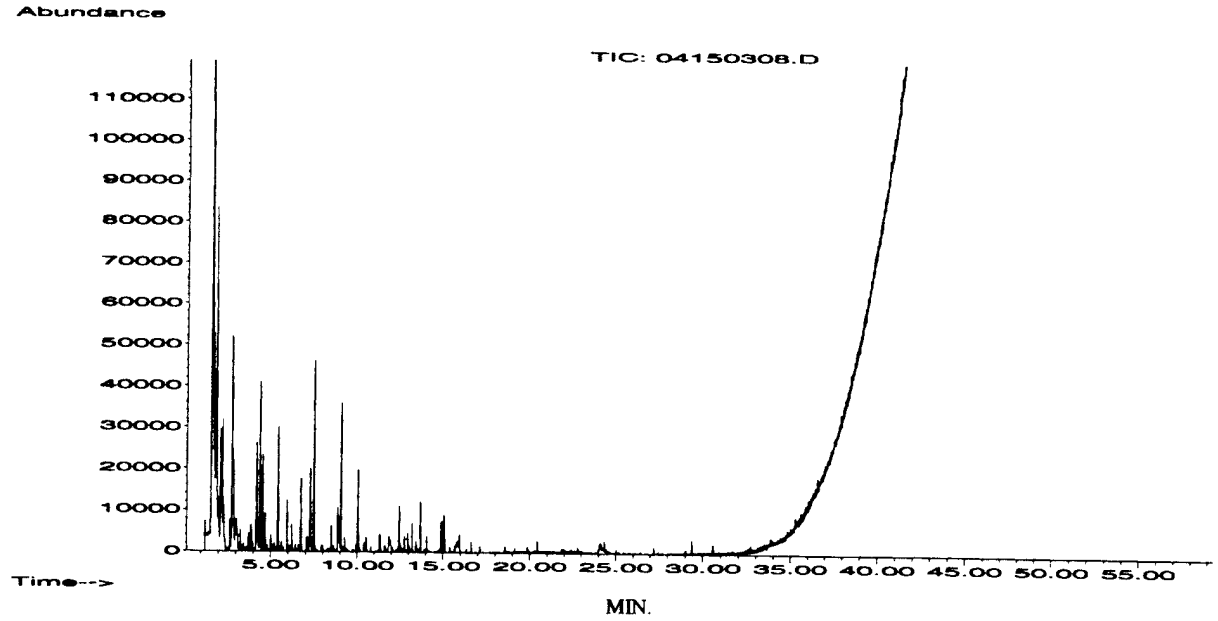



*Figure 5.* Pyrogram of cotton

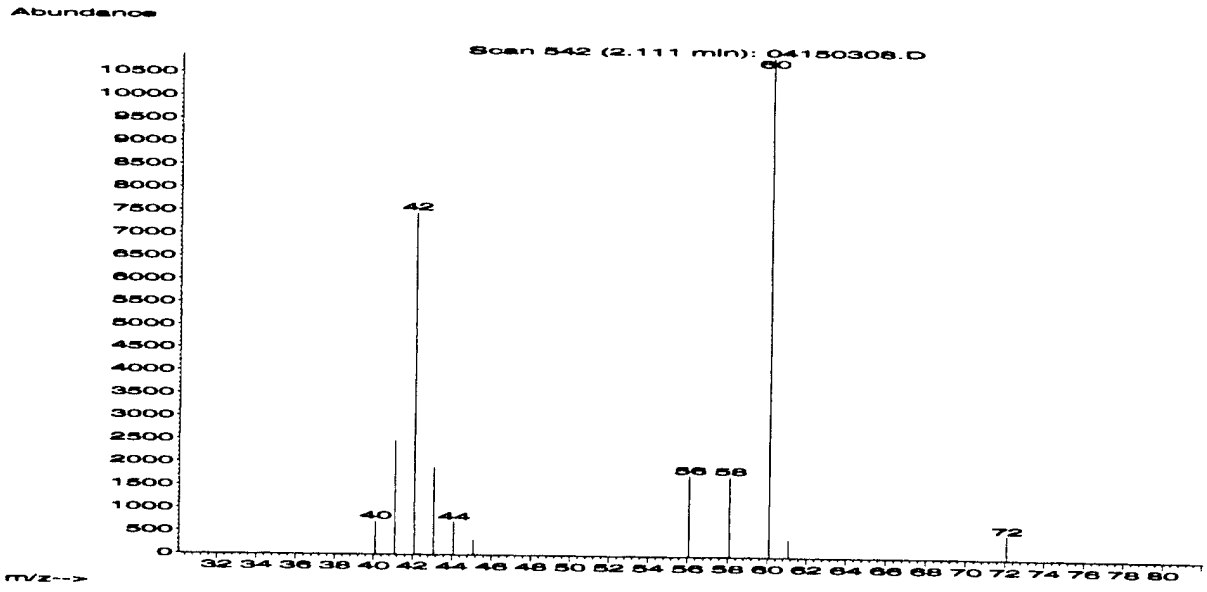



*Figure 6.* Mass spectrum of glycolaldehyde

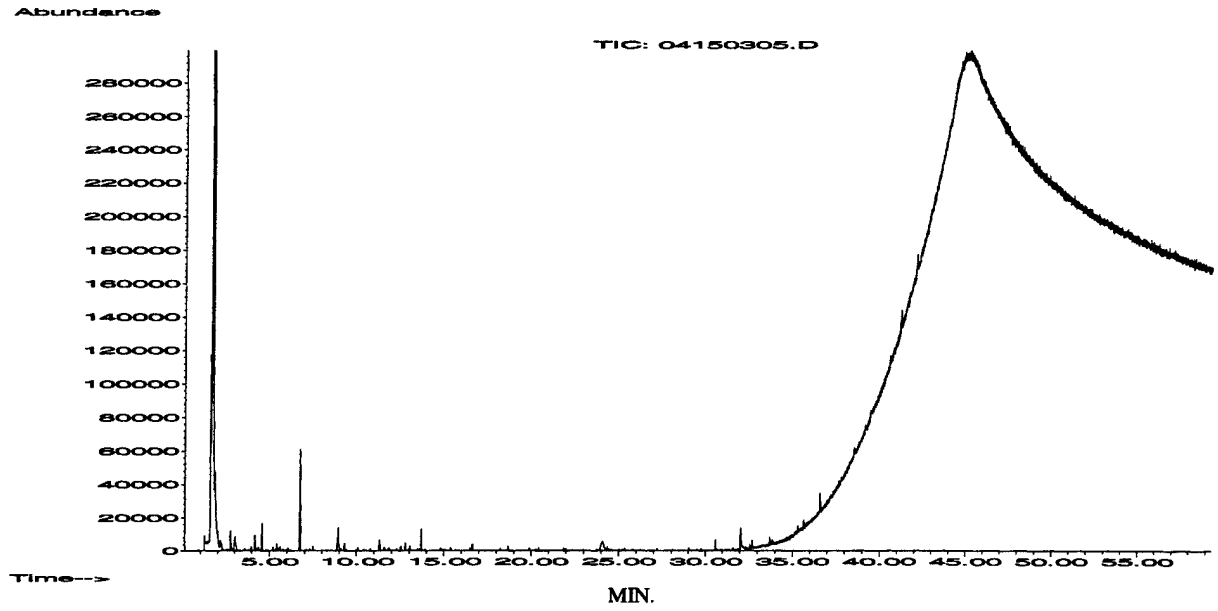



*Figure 7.* Pyrogram of Gore-tex

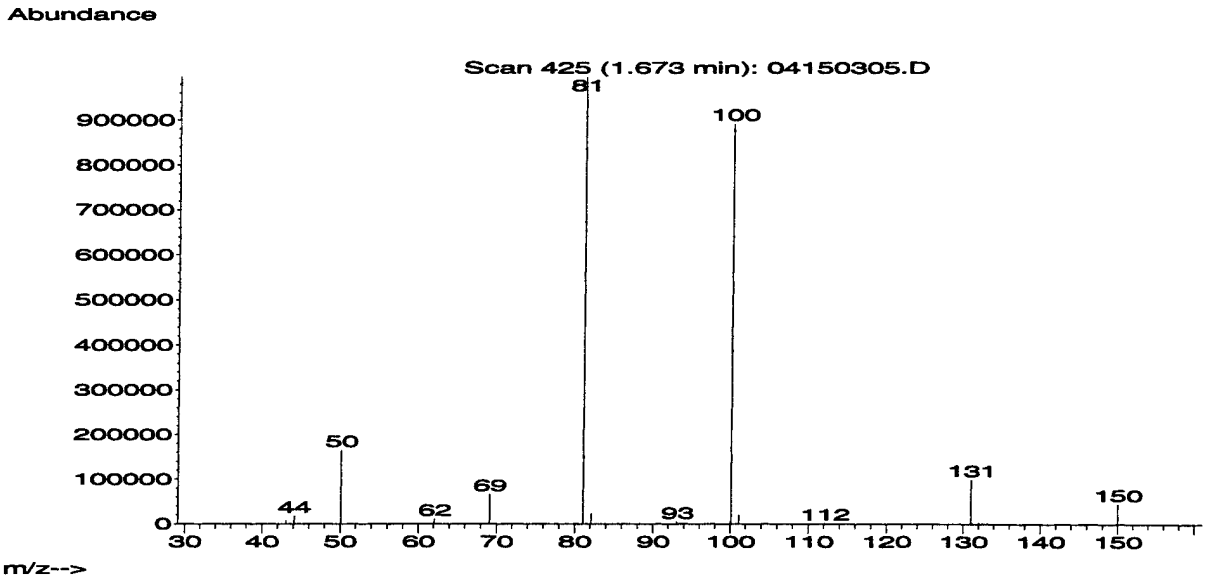



*Figure 8.* Mass spectrum of tetrafluoroethylene

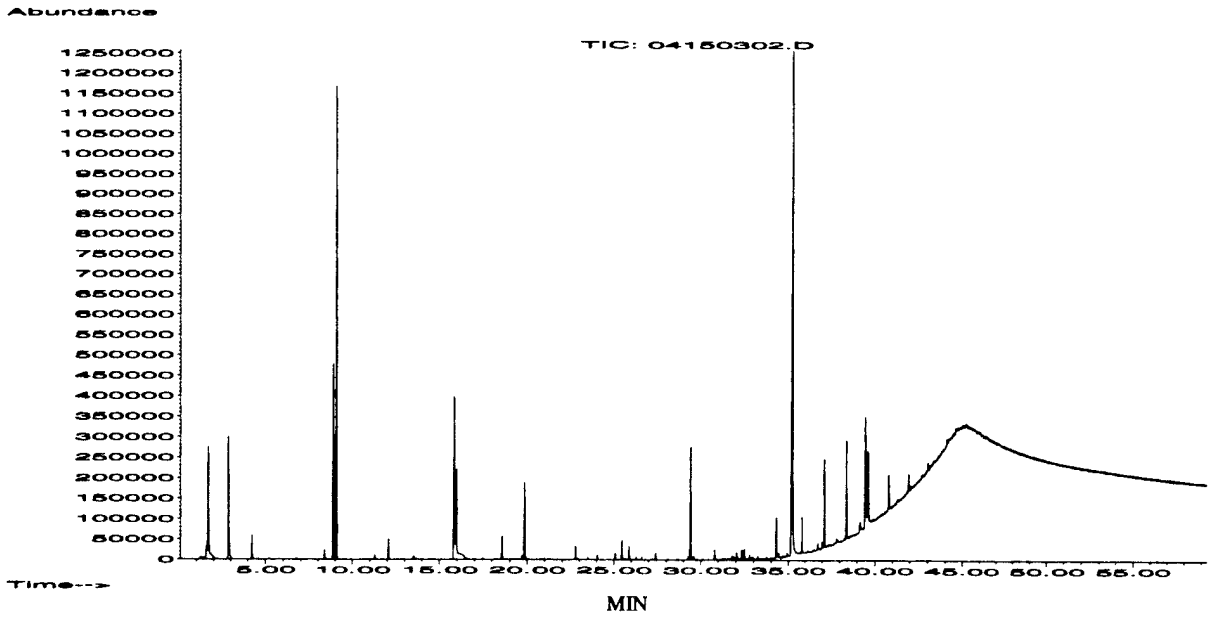



*Figure 9.* Pyrogram of Kevlar®

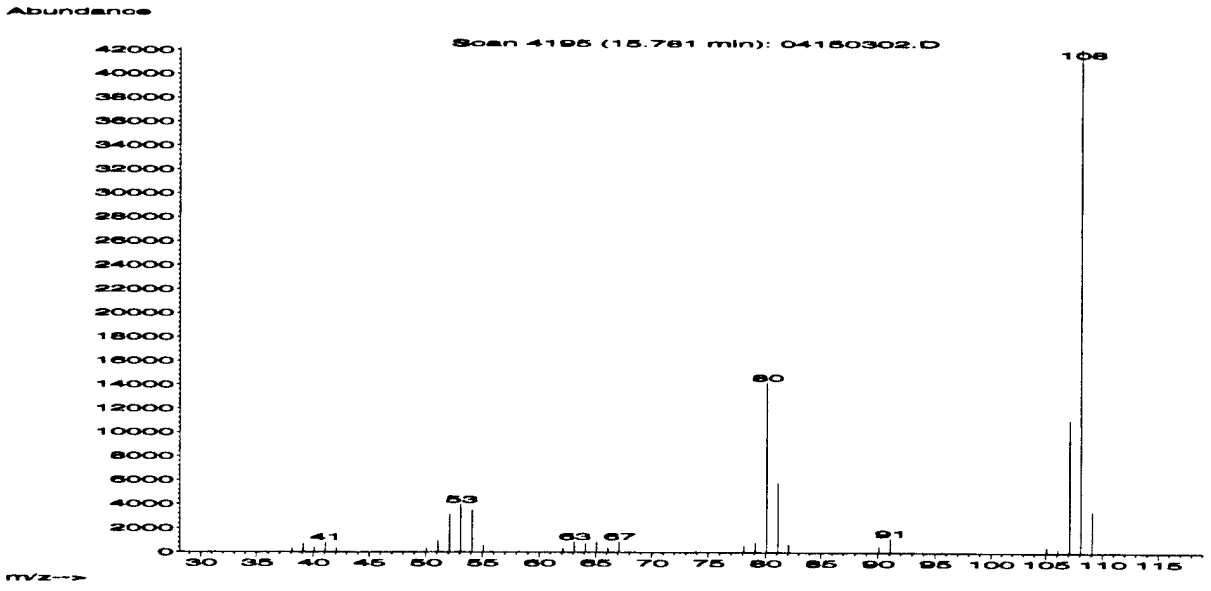



*Figure 10.* Mass spectrum of 1,4-diaminobenzene

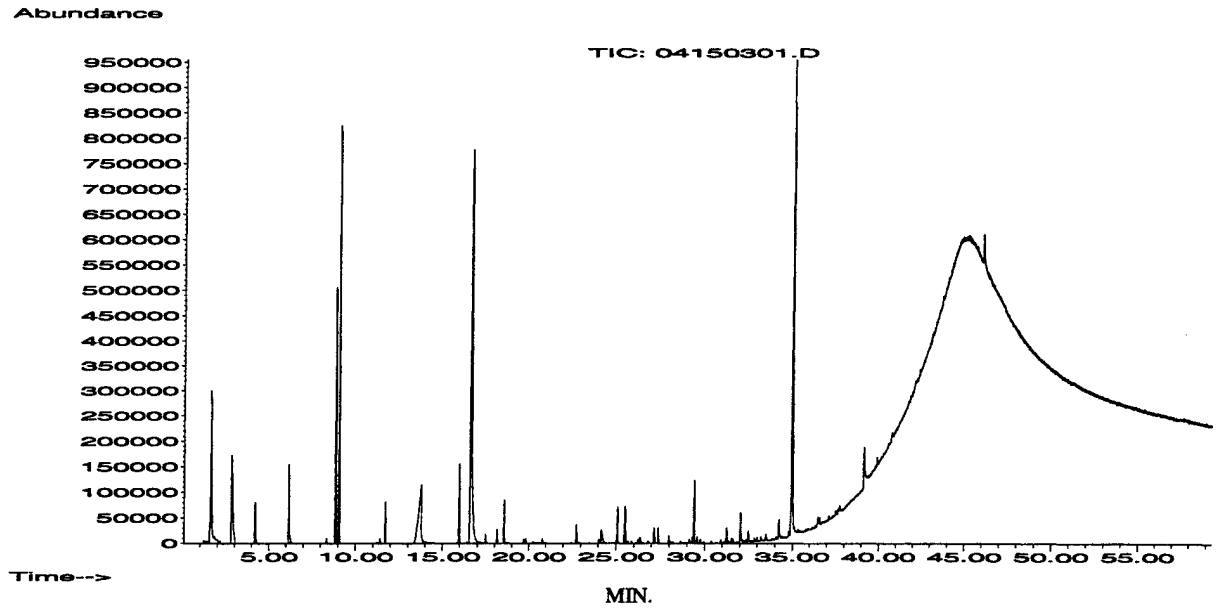



*Figure 11.* Pyrogram of Nomex®

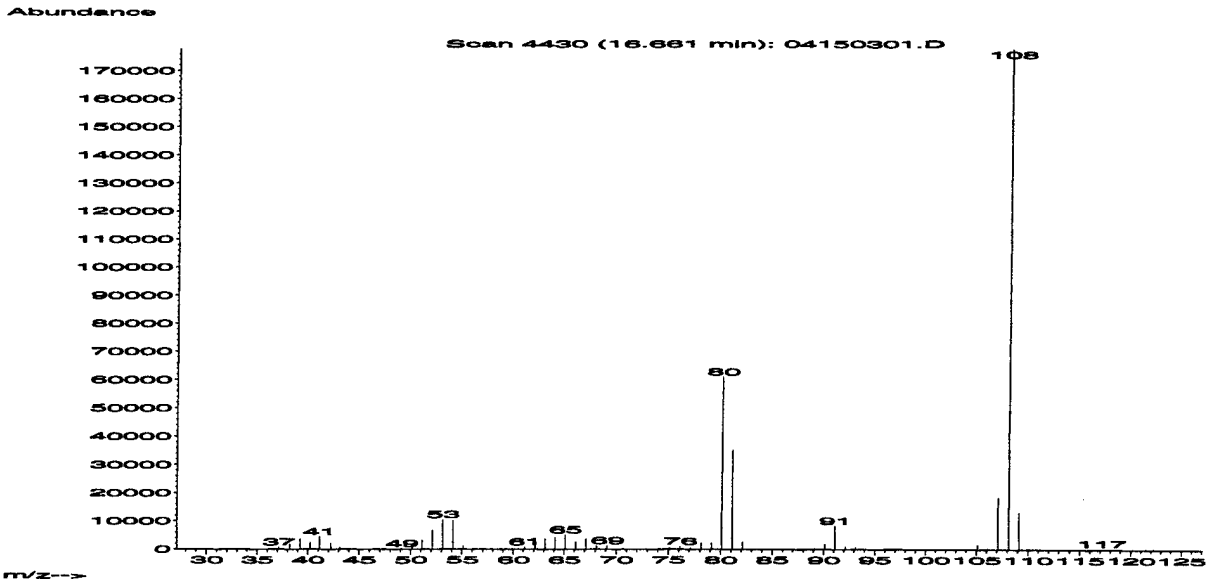



*Figure 12.* Mass spectrum of 1,3-diaminobenzene

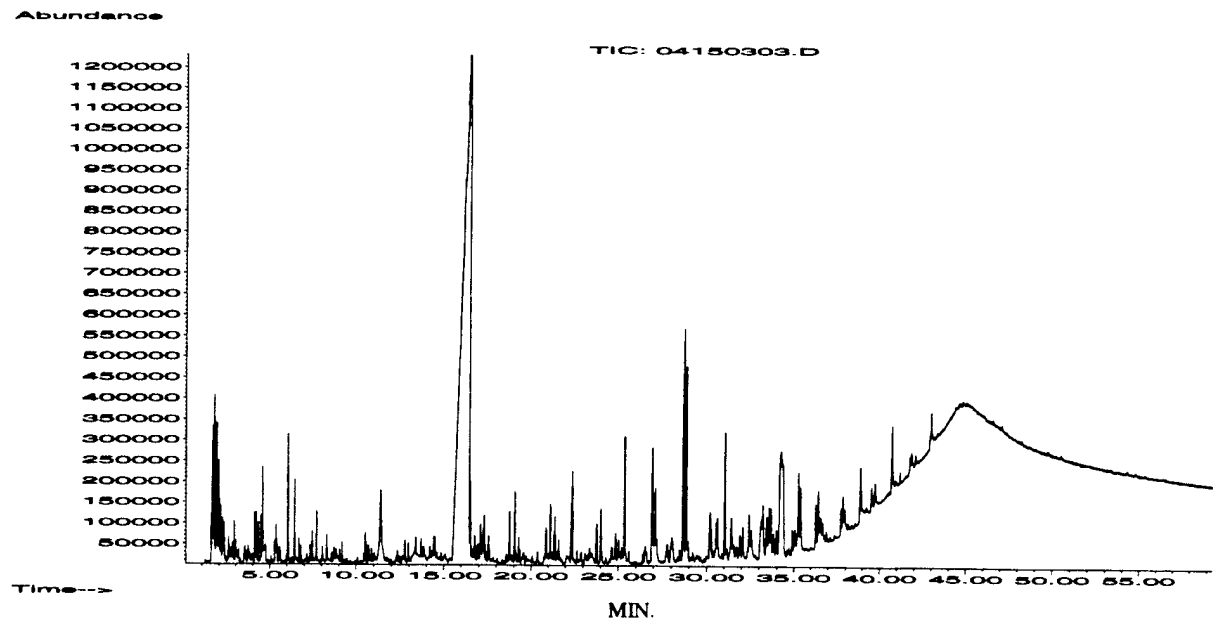



*Figure 13.* Pyrogram of nylon 6

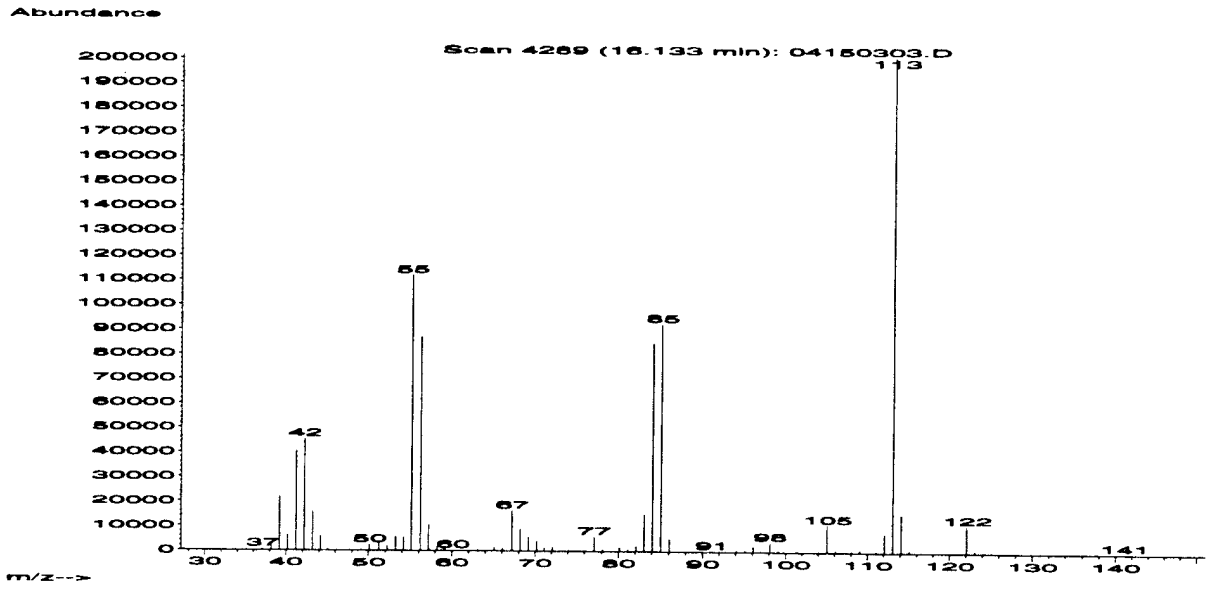



*Figure 14.* Mass spectrum of caprolactam

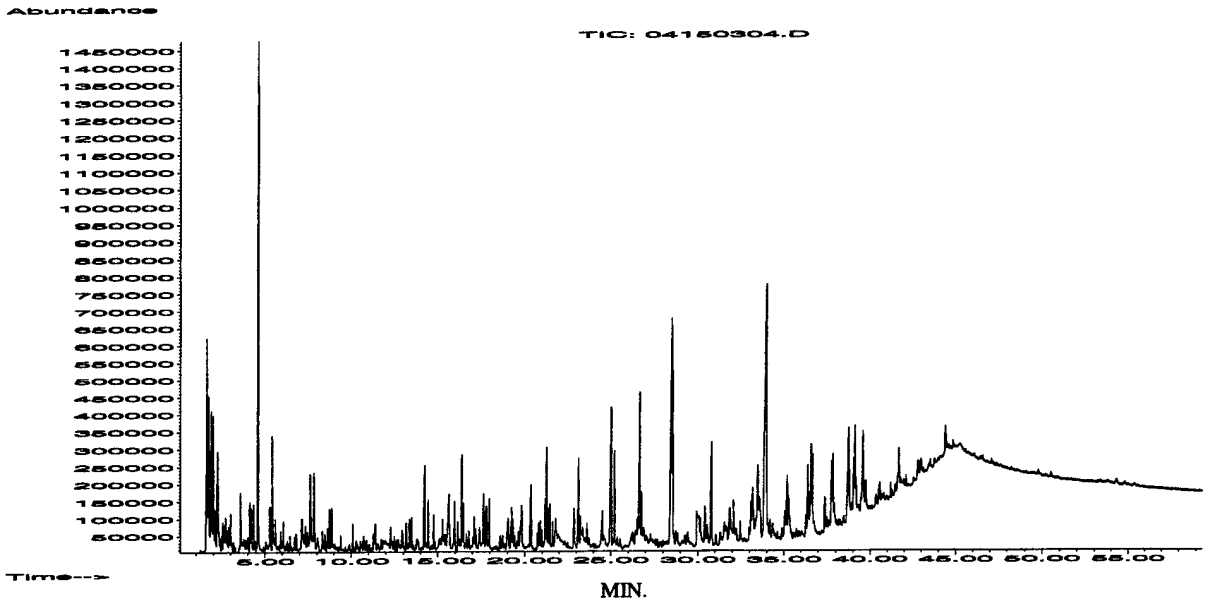



*Figure 15.* Pyrogram of nylon 66

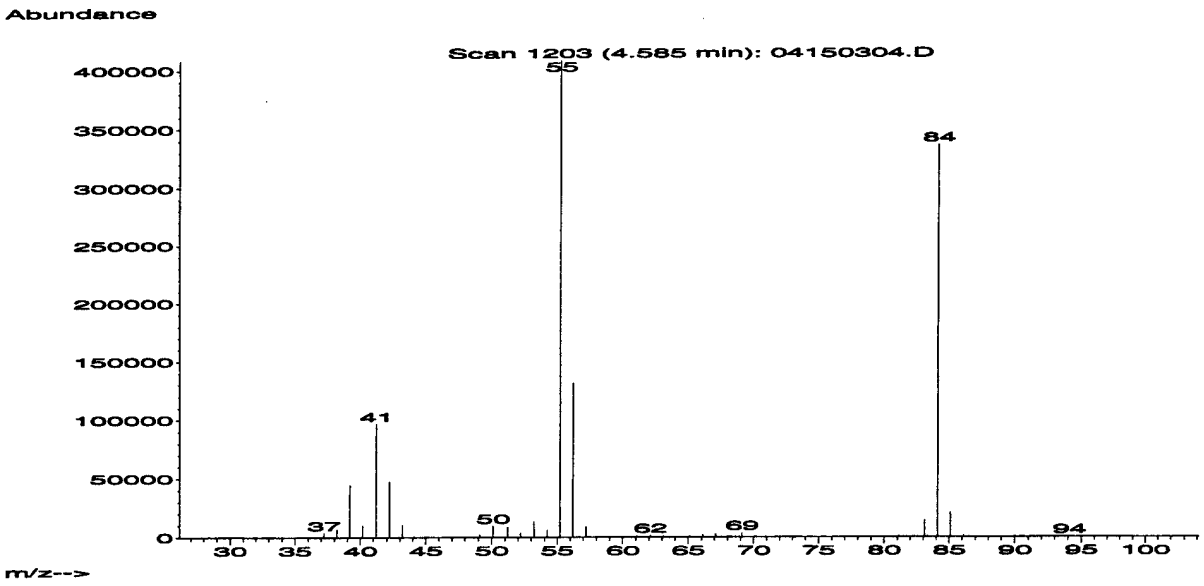



*Figure 16.* Mass spectrum of cyclopentanone

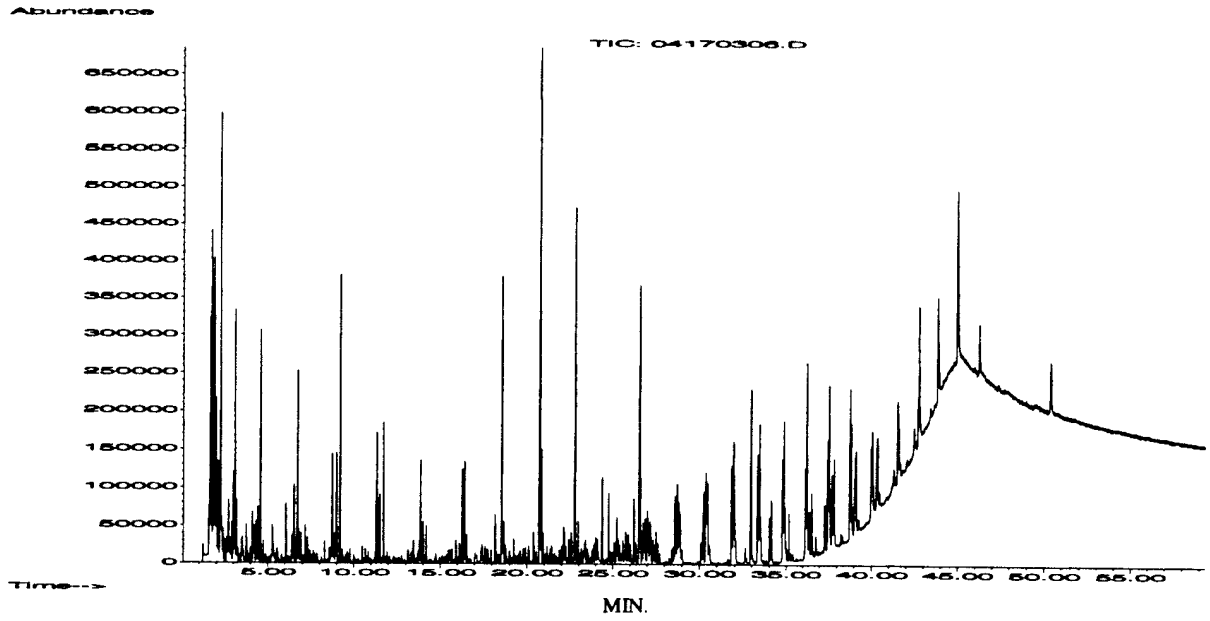



*Figure 17.* Pyrogram of nylon 12

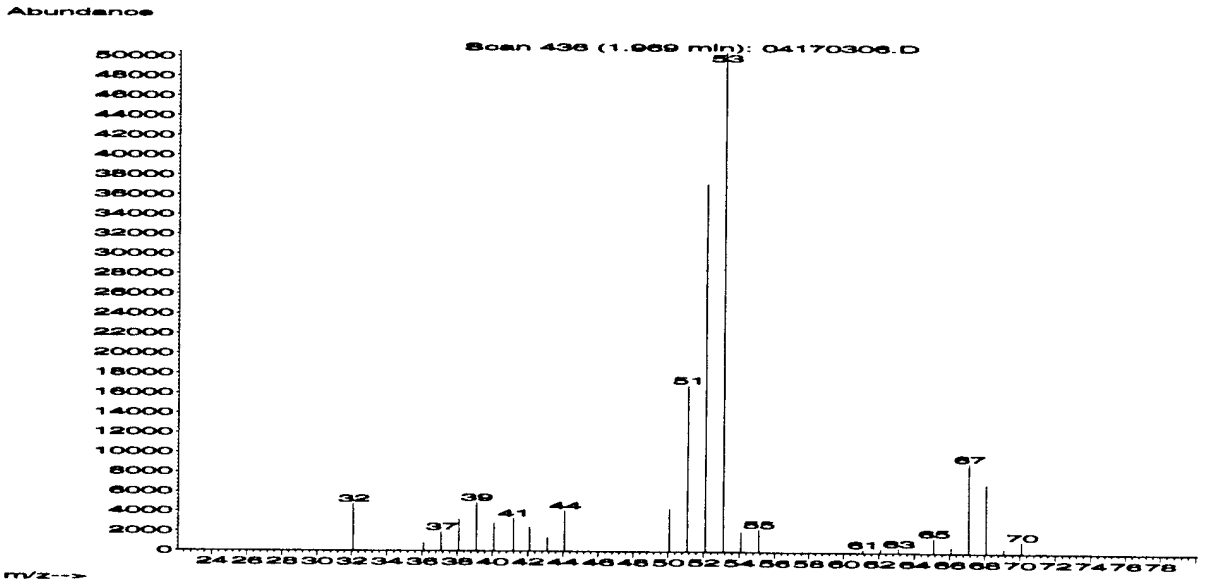



*Figure 18.* Mass spectrum of 2-propenenitrile

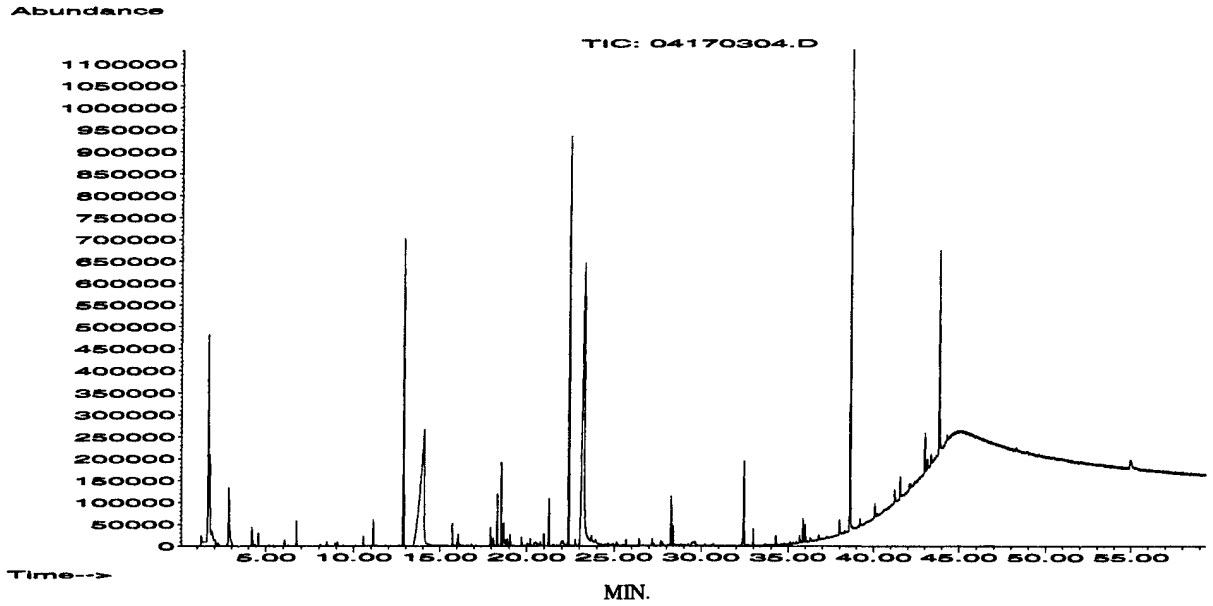



*Figure 19.* Pyrogram of polyester

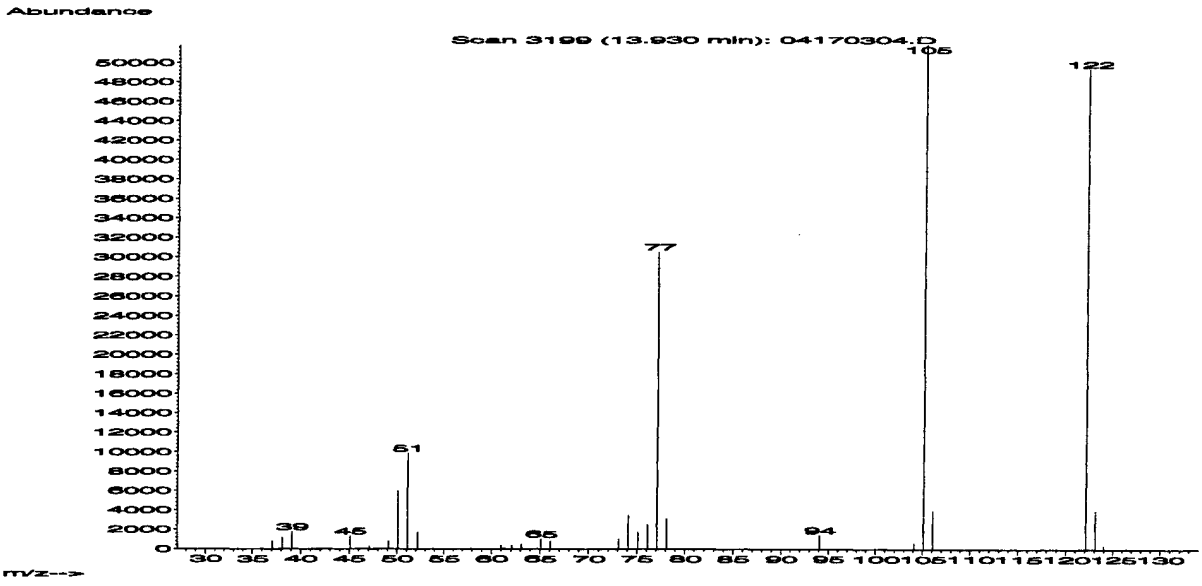



*Figure 20.* Mass spectrum of benzoic acid

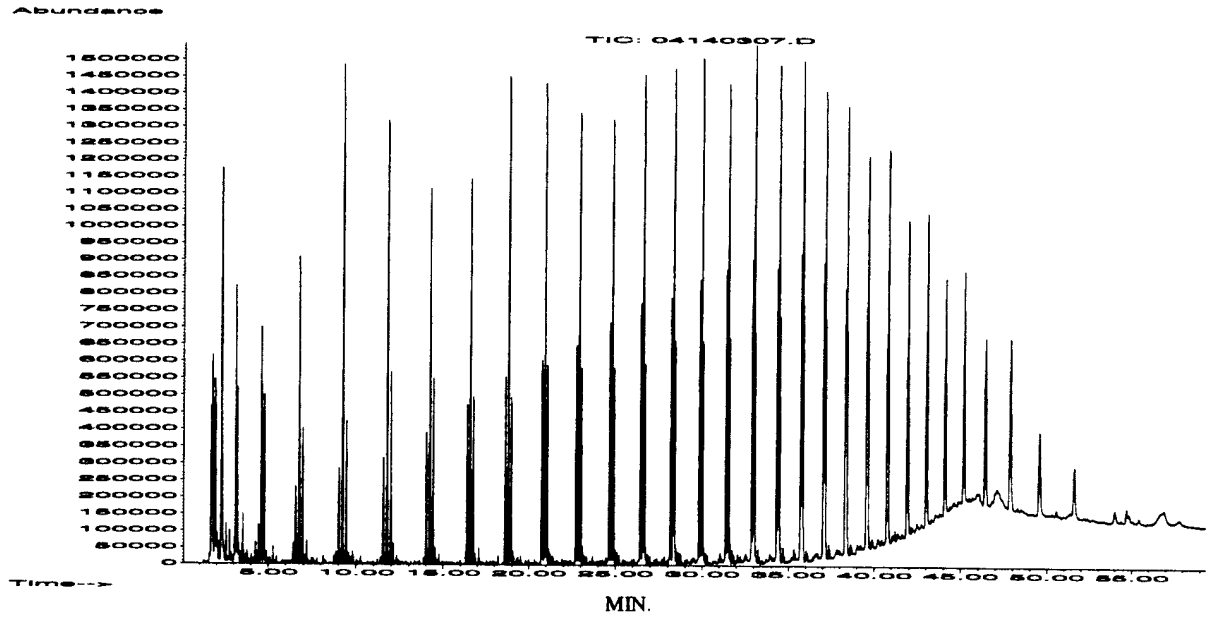



*Figure 21.* Pyrogram of polyethylene

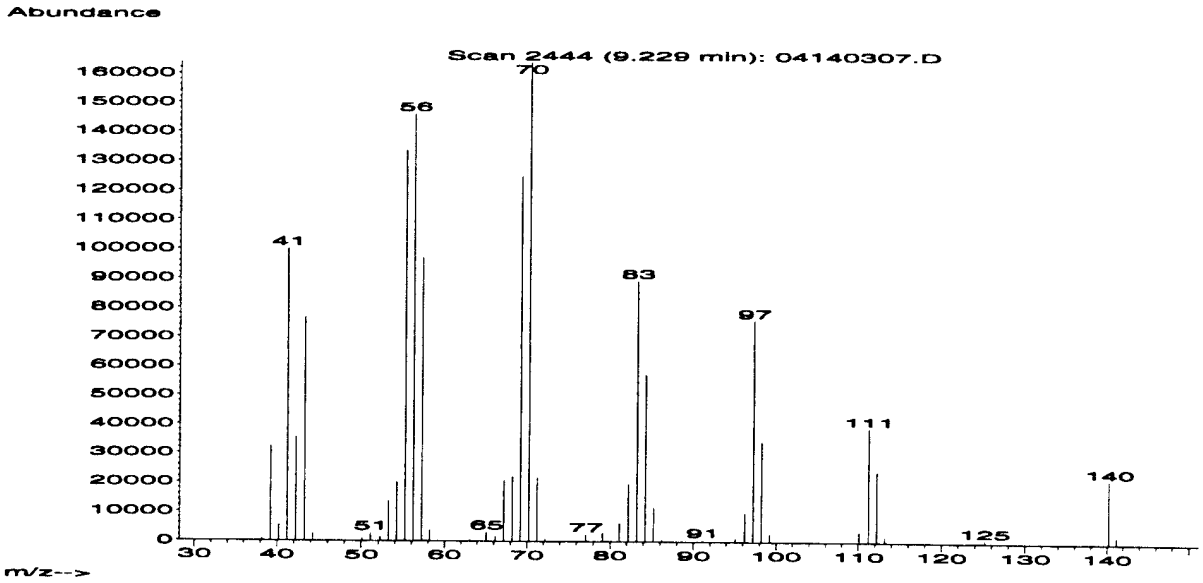



*Figure 22.* Mass spectrum of decene

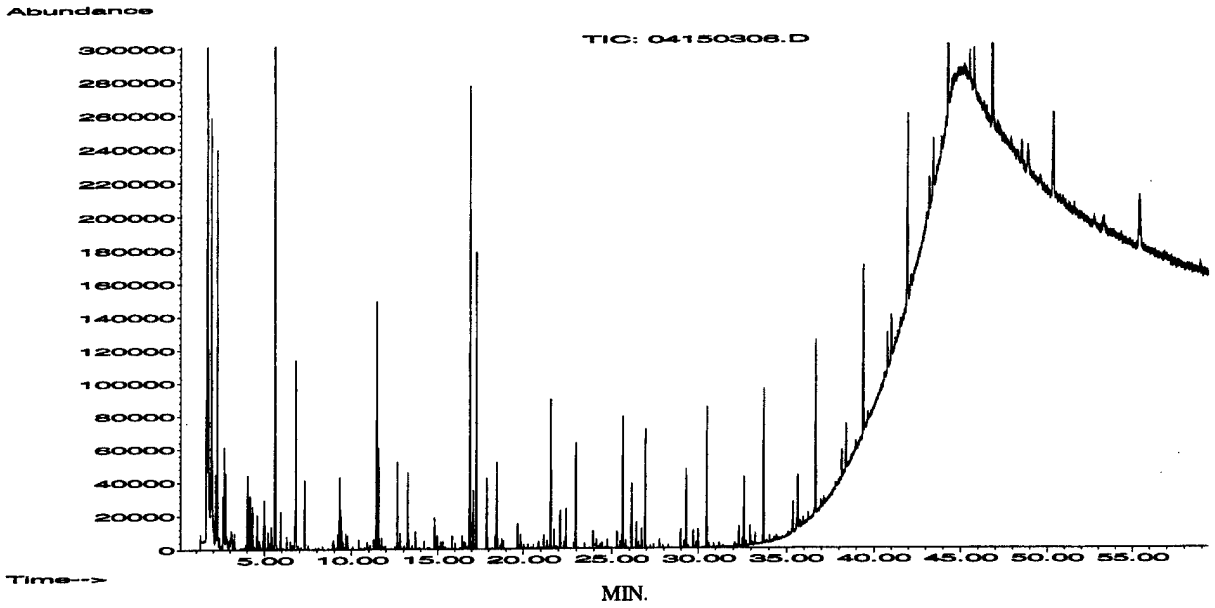



*Figure 23.* Pyrogram of polypropylene

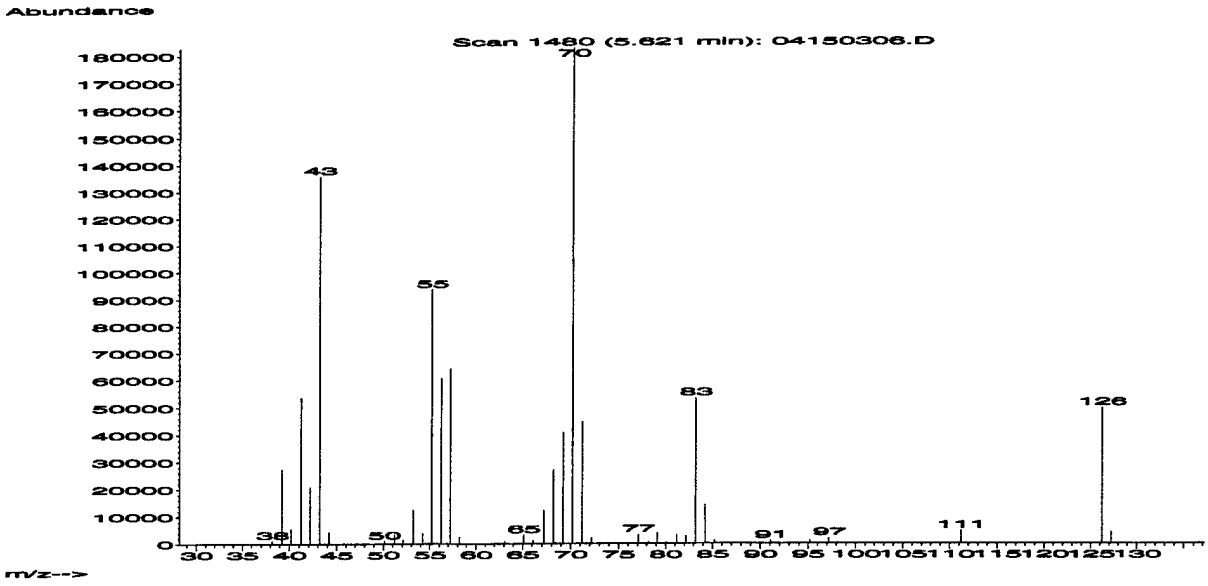



*Figure 24.* Mass spectrum of 2,4-dimethyl-1-heptene

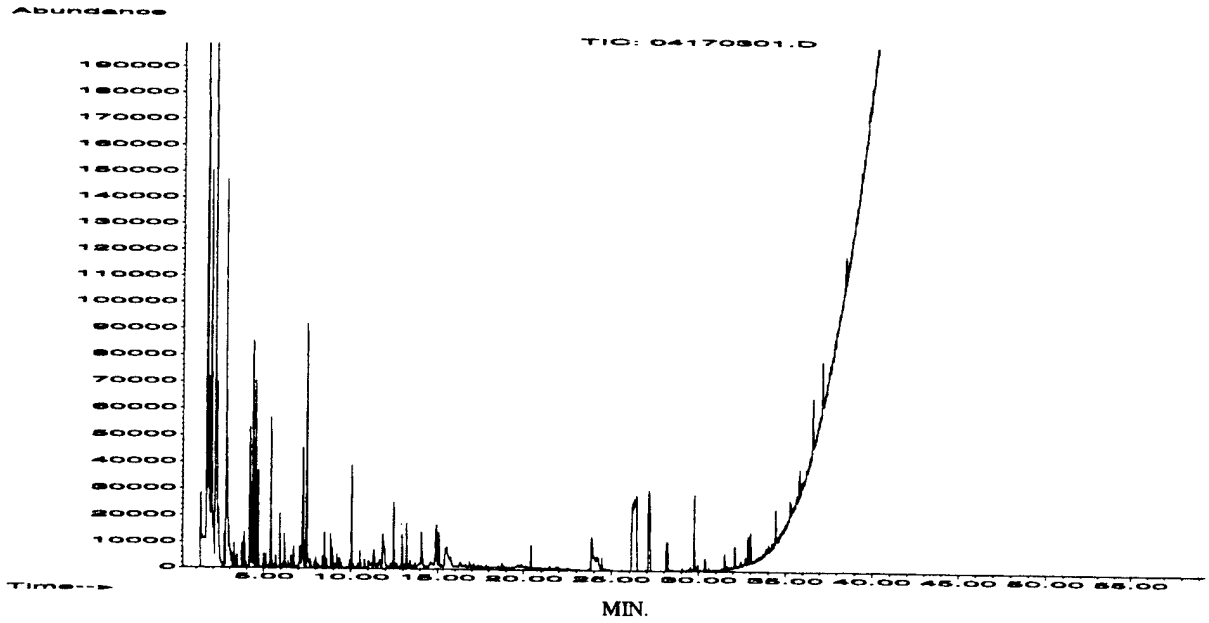



*Figure 25.* Pyrogram of rayon

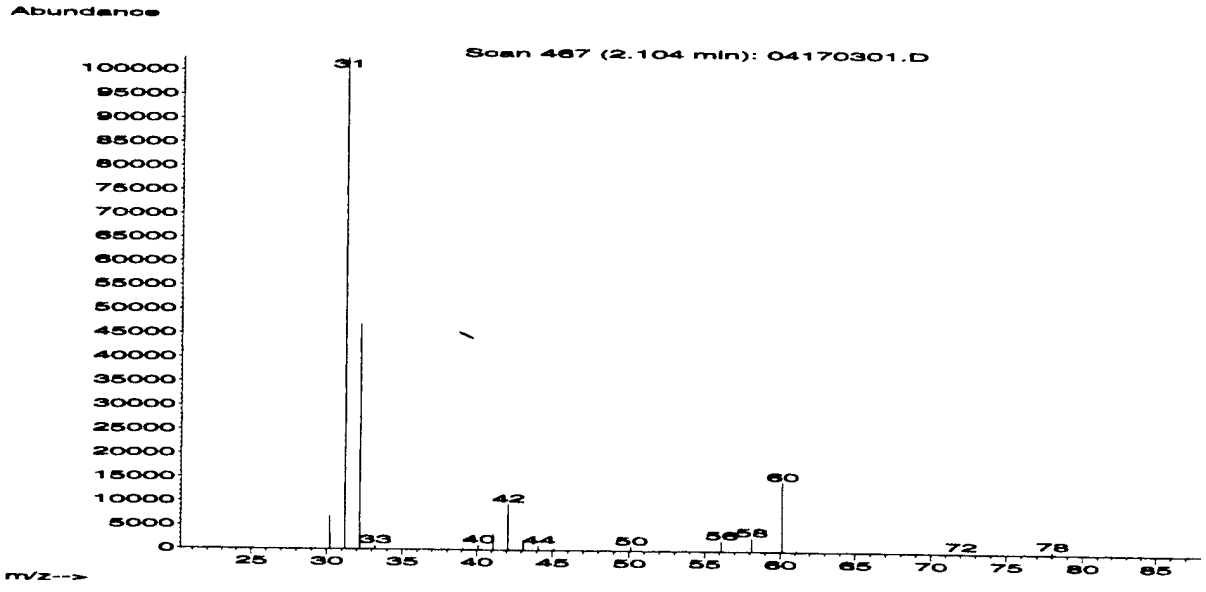



*Figure 26.* Mass spectrum of gycolaldehyde

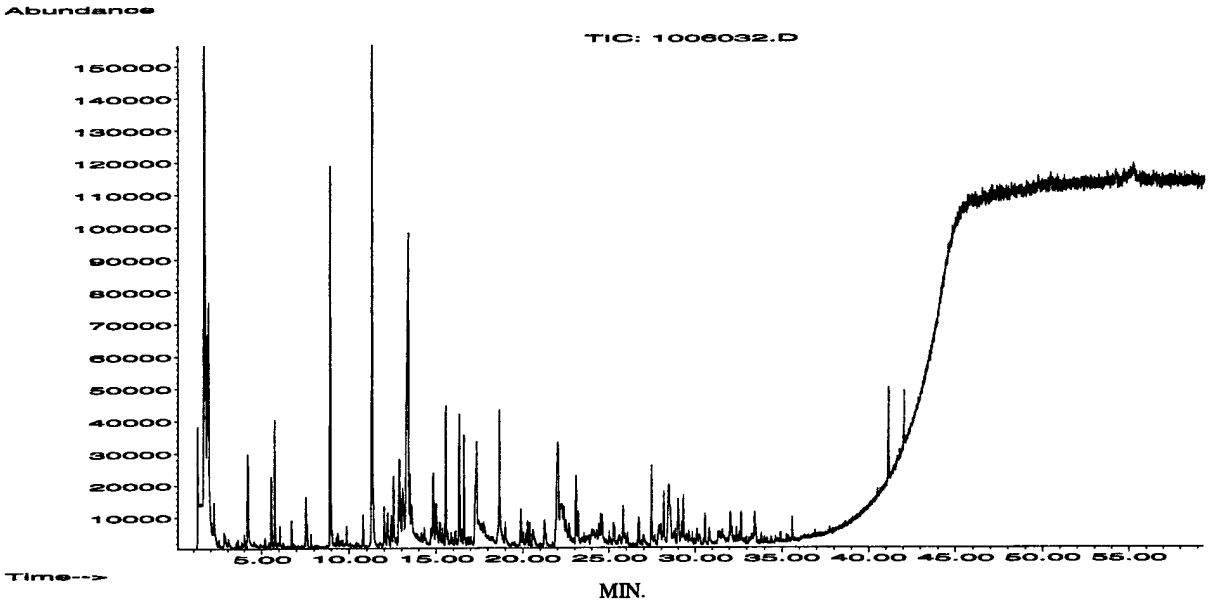



*Figure 27.* Pyrogram of silk

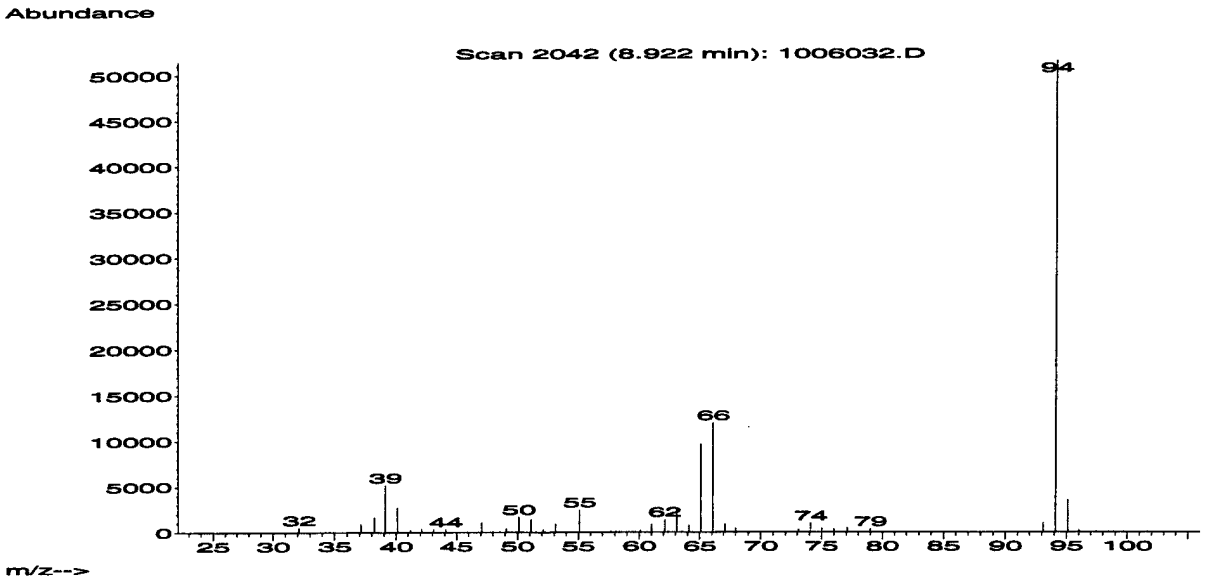



*Figure 28.* Mass spectrum of phenol

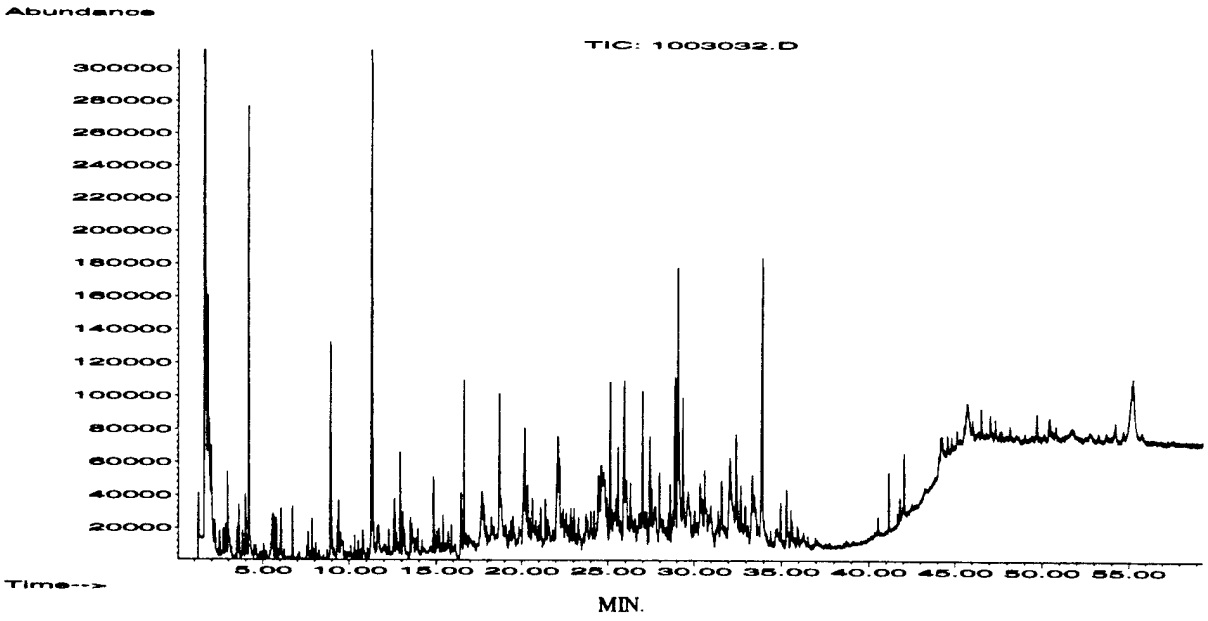



*Figure 29.* Pyrogram of wool

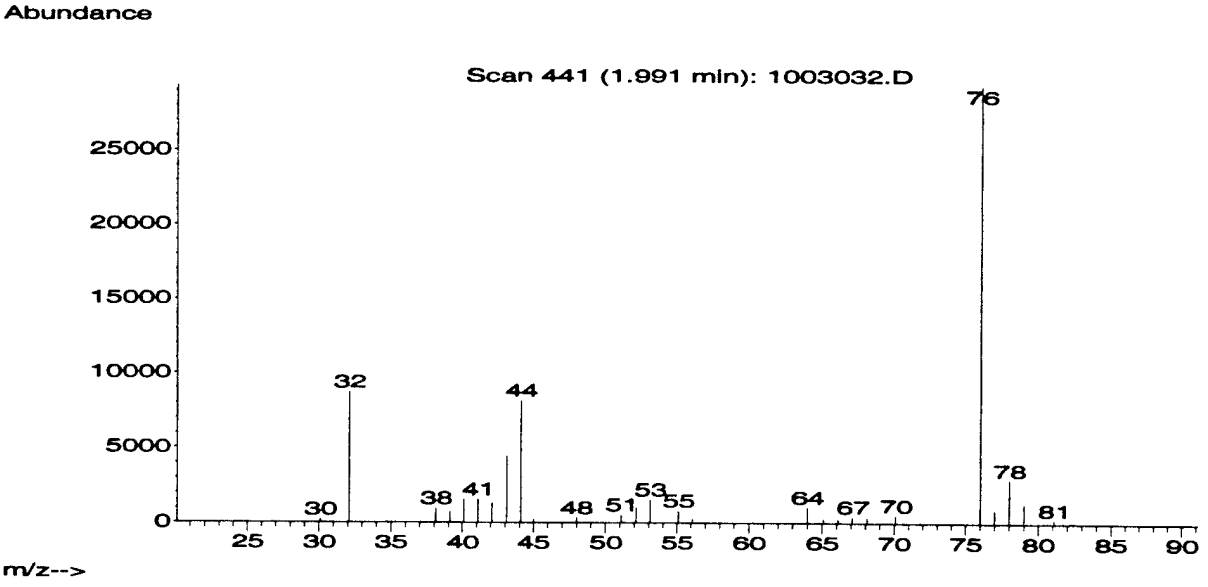



*Figure 30.* Mass spectrum of carbon disulfide

Figures 31 to 38 show pyrograms of samples and mass spectra of their major pyrolysis products.

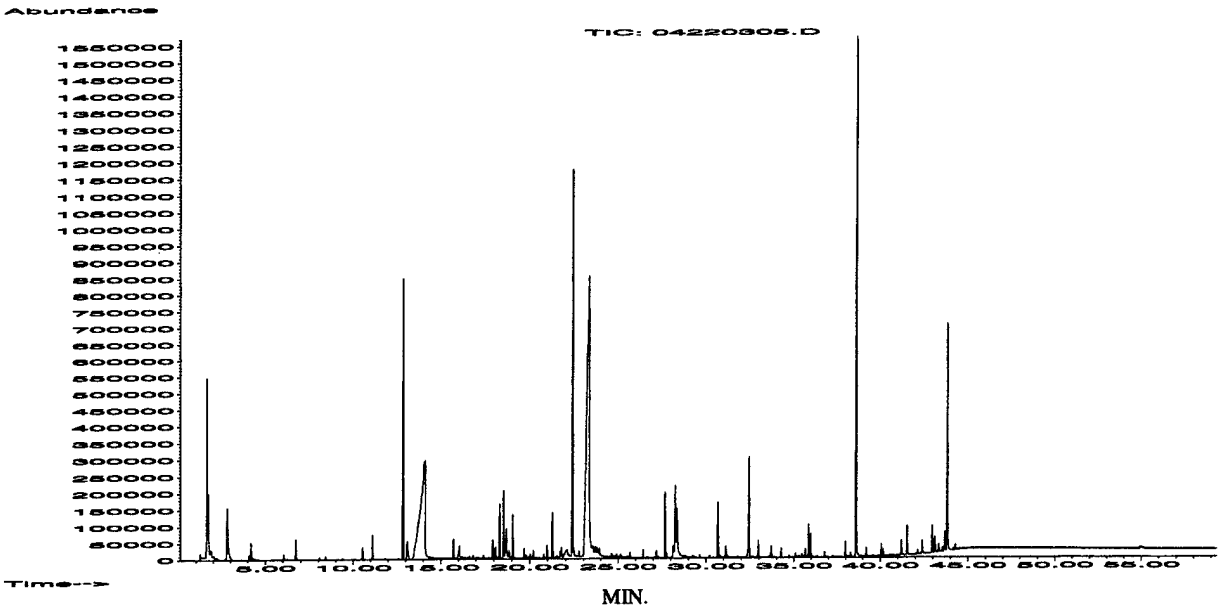



*Figure 31.* Pyrogram of an unknown fabric sample

The pyrogram above in Figure 31 and the mass spectrum in Figure 32 confirms the presence of polyester.

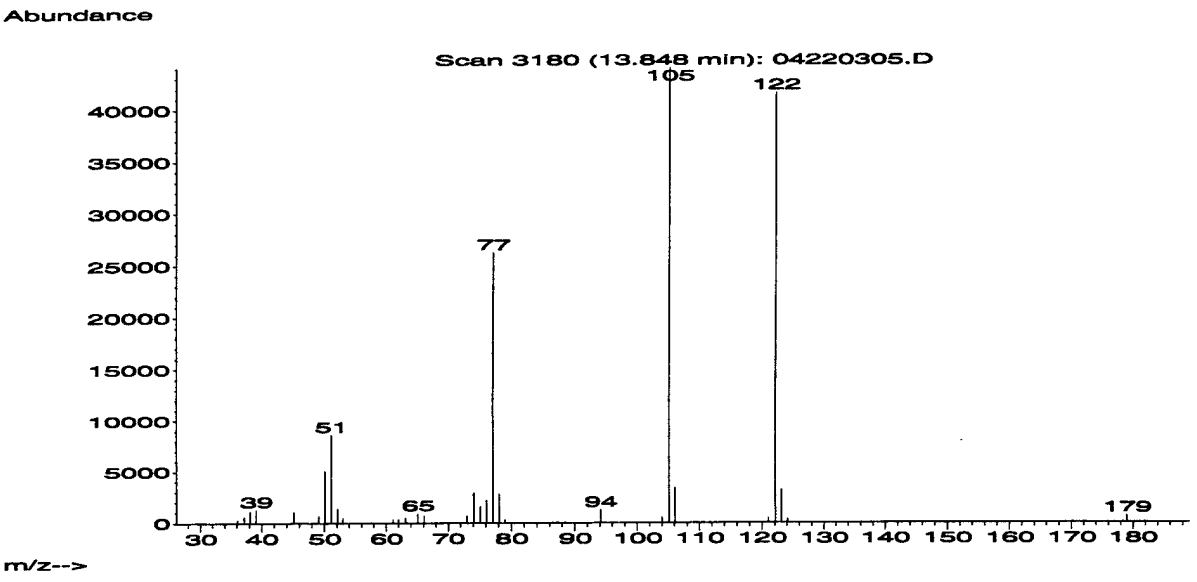



*Figure 32.* Mass spectrum of benzoic acid

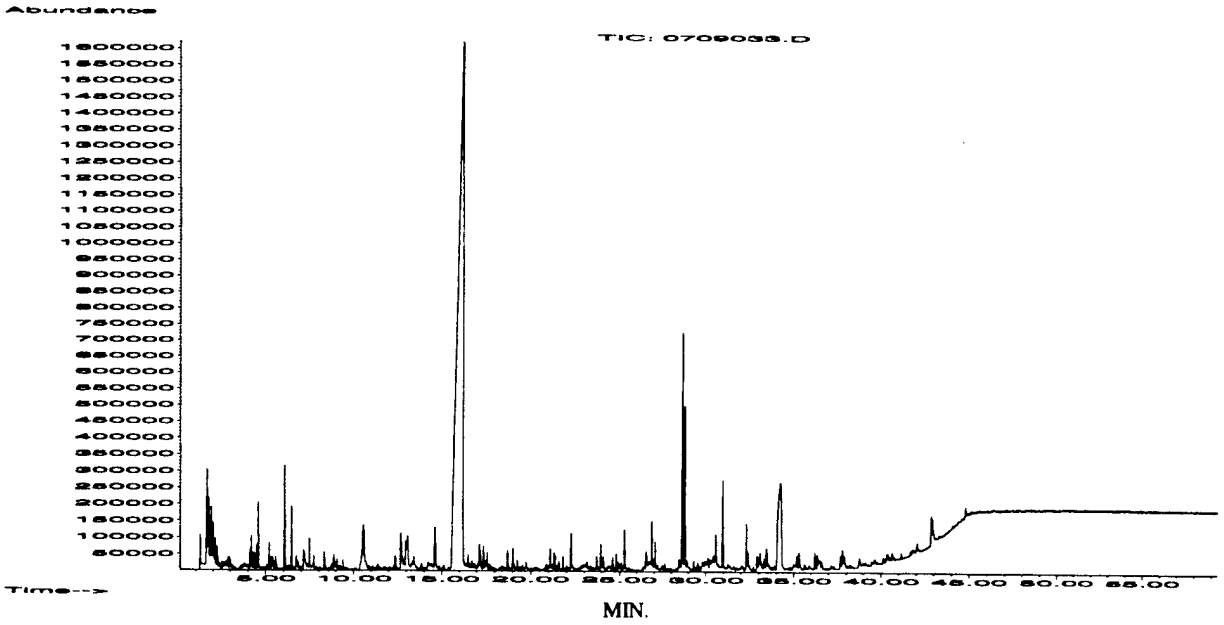



*Figure 33.* Pyrogram of an unknown helmet liner sample

The pyrogram above in Figure 33 and the mass spectrum in Figure 34 confirm the presence of nylon 6.

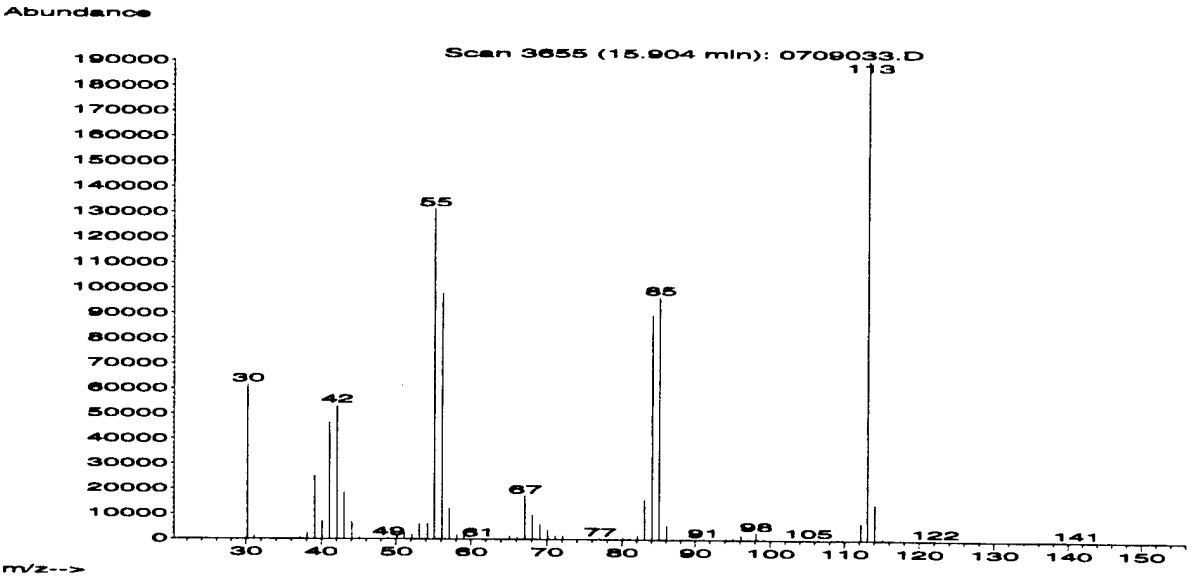



*Figure 34.* Mass Spectrum of Caprolactam

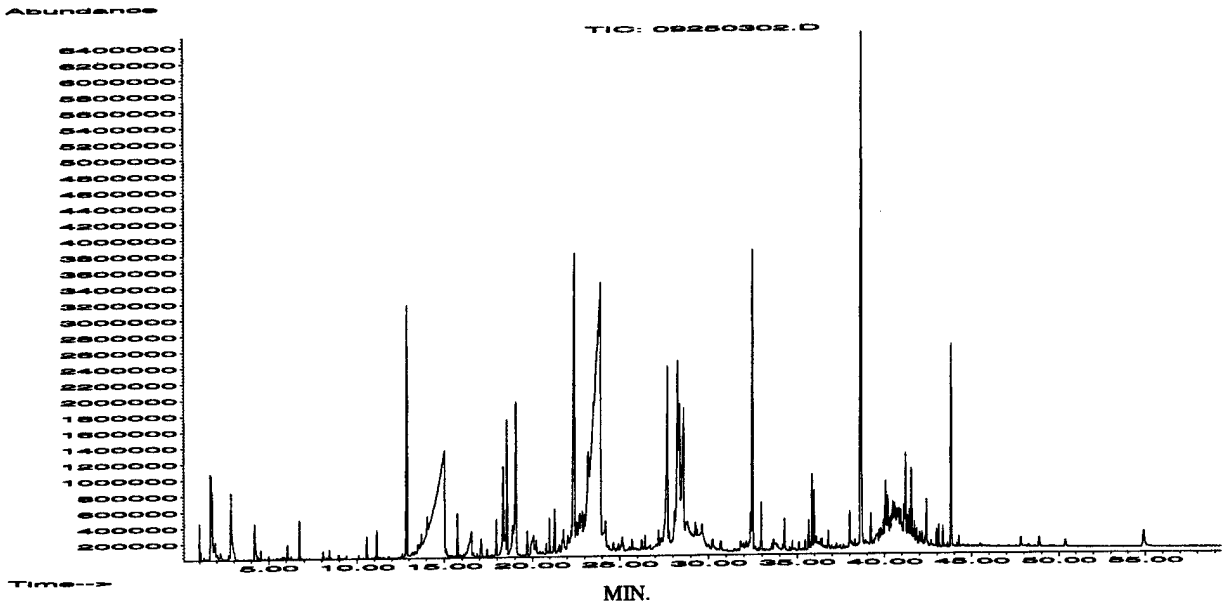



*Figure 35.* Pyrogram of an unknown tent material sample after extraction of the polyvinyl chloride (PVC)

The pyrogram above in Figure 35 and the mass spectrum in Figure 36 confirm the presence of polyester.

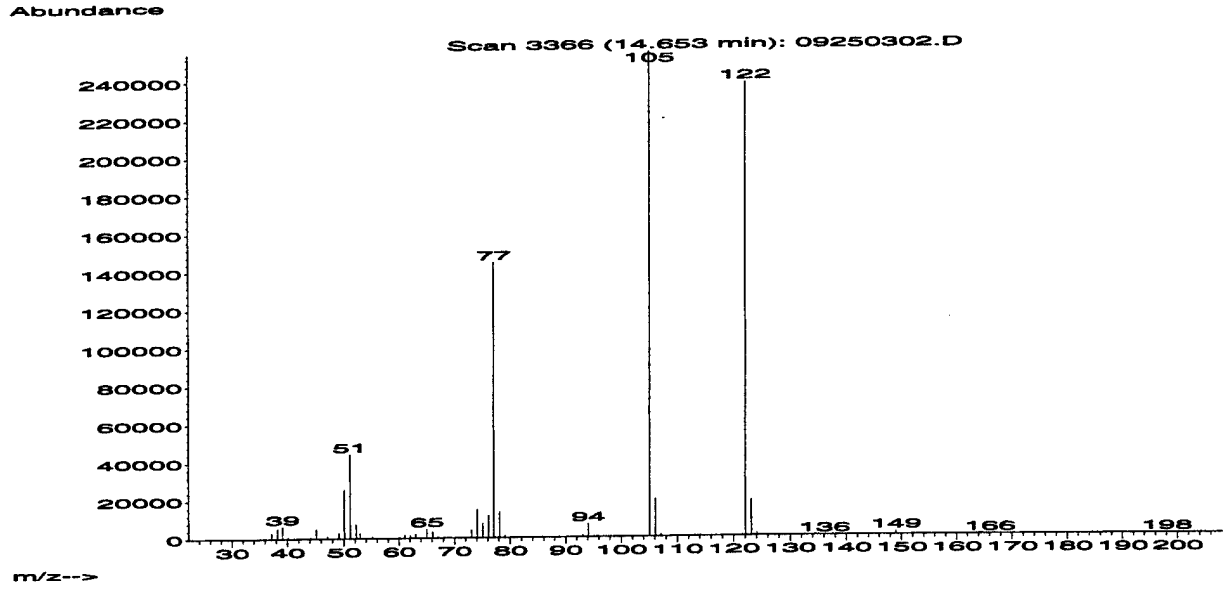



*Figure 36.* Mass spectrum of benzoic acid

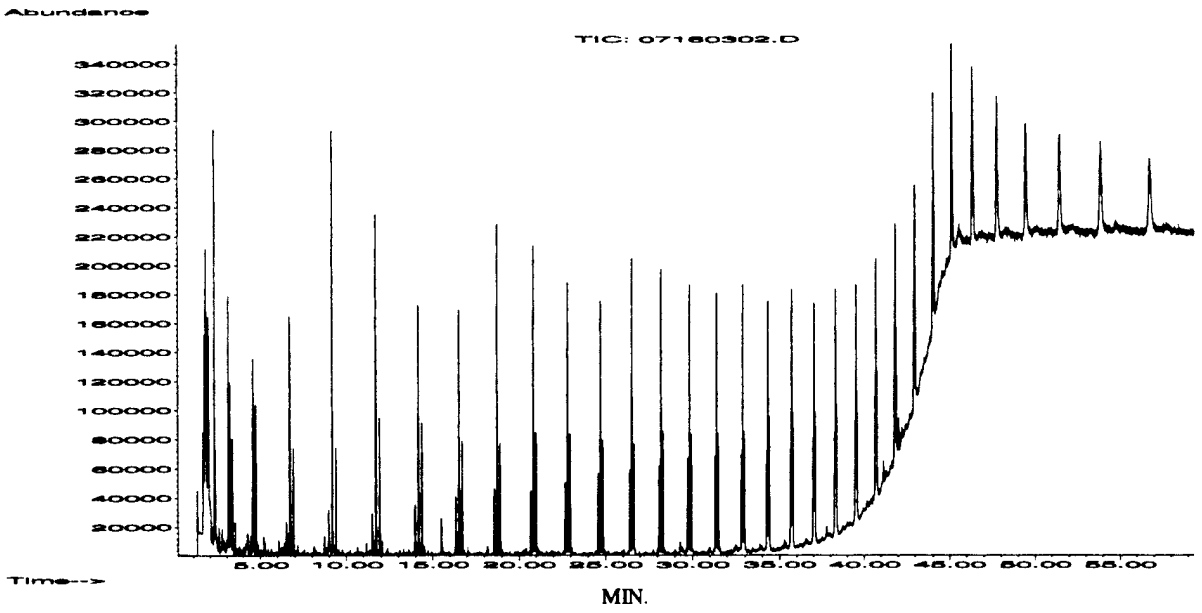



*Figure 37.* Pyrogram of an unknown foamy inner layer sample from a headgear

The pyrogram above in Figure 37 and the mass spectrum in Figure 38 confirm the presence of polyethylene.

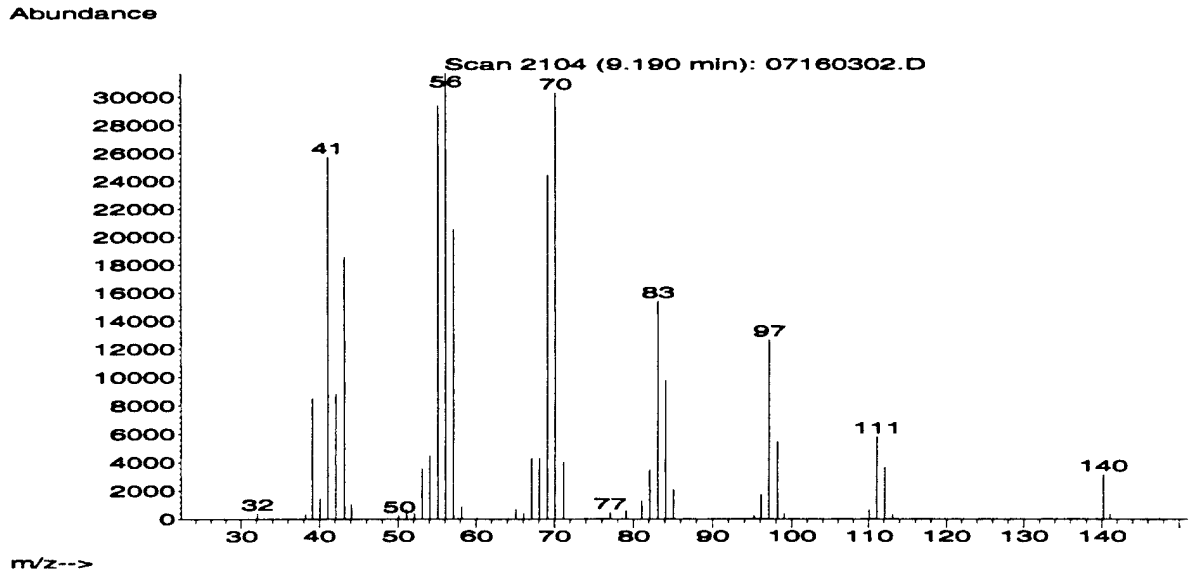



*Figure 38.* Mass spectrum of 1-decene

Not all mass spectra of major pyrolysis products are shown here because there are just too many. However, they are summarized on Tables 2 as matched with the mass spectral library showing corresponding molecular weights for the standards and on Table 3 below and Table 4 on next page for the samples.

Table 3. *Samples Identified by Py-GC*

| **Sample Number** | **Matched** Pyrogram Profile | **Major Pyrolysis Product*** | **Fiber Identified** |
|---|---|---|---|
| 8415-01-444-1169 | Nylon 66 | Cylopentanone | Nylon 66 |
| 8415-01-444-1200 | Nylon 66 | Cylopentanone | Nylon 66 |
| 8415-01-444-2325 | Nylon 66 | Cylopentanone | Nylon 66 |
| 8415-01-444-2308 | Nylon 66 | Cylopentanone | Nylon 66 |
| BL15019832 4HBF | Nylon 66 | Cylopentanone | Nylon 66 |
| BL15019832 4H | Nylon 66 | Cylopentanone | Nylon 66 |
| 090597103TOLAH | Nylon 66 | Cylopentanone | Mostly Nylon 66 |
| 090597103TOWHBF | Nylon 66 | Cylopentanone | Mostly Nylon 66 |
| 090597103TOWH | Nylon 66 | Cyclopentanone | Mostly Nylon 66 |
| BL261197232TOPBH | Nylon 66 | Cyclopentanone | Mostly Nylon 66 |
| BL261197232TOBHW | Nylon 66 | Cyclopentanone | Mostly Nylon 66 |
| BL261197232TOWEB | Nylon 6 | Caprolactam | Nylon 6 |
| BL261197232TOW | Nylon 66 | Cyclopentanone | Mostly Nylon 66 |
| B212059729OCP1J | Nylon 66 | Cyclopentanone | Mostly Nylon 66 |
| 1JHBNA2AUTOCLAV | Nylon 66 | Cyclopentanone, etc. | Nylon 66 + |
| P1P11P1030991HBP | Nylon 66 | Cyclopentanone, etc. | Nylon 66 + |
| P1P11P1030991HBR | Nylon 66 | Cyclopentanone, etc. | Nylon 66 + |
| P1P11P1030991HRP | Nylon 66 | Cyclopentanone, etc. | Nylon 66 + |
| P1P11P1030991SHP | Nylon 66 | Cyclopentanone, etc. | Nylon 66 + |
| 016F1601 | Rayon | Not identified | Rayon |
| 011F0111 | Polyester | Benzoic Acid | Polyester |
| 015F0101 | Nylon 66 | Cyclopentanone | Nylon 66 |
| MEMB0019 | Polyethylene | 3 Hydrocarbons | Polyethylene |
| PM000001 | Polyester | Benzoic Acid | Polyester |

* The major pyrolysis product was identified by position and height on the pyrogram as identified on references. The fiber was identified by pyrogram profile comparison of sample to those of standards.

Table 4. *Samples Identified by Py-GC-MS*

| Sample Number | Matched Pyrogram Profile | Major Pyrolysis Product(s) & Mol. Wt. | Fiber Identified |
|---|---|---|---|
| 04220302 | Acrylic | Acrylonitrile - 53 | Acrylic |
| 04220303 | Nylon 66 | Cylopentanone - 84 | Nylon 66 |
| 04220305 | Polyester | Benzene - 78<br>Benzoic acid - 122 | Polyester |
| 070803 | Nylon 6 | Caprolactam - 113 | Nylon 6 |
| 0709031 | Polyester | Benzoic acid - 122<br>Biphenyl - 154 | Polyester |
| 0709032 | Polyester | Benzoic Acid - 122<br>Biphenyl - 154 | Polyester |
| 0709033 | Nylon 6 | Caprolactam - 113 | Nylon 6 |
| 07160301 | Polyethylene | 1-Decene - 140<br>Decane - 142 | Polyethylene |
| 07160302 | Polyethylene | 1,9-Decadiene - 138<br>1-Decene - 140<br>Decane - 142 | Polyethylene |
| 07160303 | Nylon 66 | Cyclopentanone - 84 | Nylon 66 |
| 07160304 | Nylon 6 | Caprolactam - 113 | Nylon 6 |
| 9250301 | Polyester | Benzene - 78<br>Benzoic Acid - 122<br>Biphenyl -154 | Polyester |
| 9250302 | Polyester | Benzene - 78<br>Benzoic acid -122 | Polyester |

## Conclusions

The addition of the mass spectrometer to the GC has expanded our capability to identify unknown fibers. When MS is used in conjunction with Py-GC, more conclusive results can be obtained in identifying unknown materials.

A pyrogram is considered a "fingerprint" of a certain fiber. It is very much reproducible as long as the conditions are kept constant. Additionally, when a major peak(s) from the pyrolysis of a sample is/are identified by mass spectrometry to be the same as that/those of the standard, there is no more doubt that they are the same fibers.

Py-GC-MS is an excellent tool for the characterization of fibers used in military materials and has allowed a more thorough analysis of fibers/fabrics used in military applications.

This document reports research undertaken at the U.S. Army Research, Development and Engineering Command, Natick Soldier Center, Natick, MA, and has been assigned No. NATICK/TR-04/011 in a series of reports approved for publication.

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